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LXXI. *Ionization Measurements of γ-Rays.*

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1. *Introduction.*

MEASUREMENTS on γ-rays can only be carried out by measuring some property of the secondary β-rays they release from matter. Various properties are available, and, in particular, the most direct information is yielded by measurements of the number [1], [2] or the energy [3] of the β-rays; but such experiments, owing to their length and difficulty, are not available for a great deal of the work on γ-rays. The work has largely been carried out by measurement of the ionization produced in the gas in a chamber, and thus it is of great importance to consider what meaning may be attached to such measurements.

Since the ionization is a tertiary effect, being produced by the secondary β-rays, it is clear that ionization measurements cannot be expected to give direct information about the primary γ-rays. Though it has long been recognized, *e.g.* by Bragg [4] in 1910, that ionization from γ-rays is a complex phenomenon, yet many workers have, in default of other data, been forced to assume that ionizations measure either number of quanta [*e.g.* Ahmad [5], Kohlrausch [6], etc.]

* Communicated by Sir E. Rutherford, P.R.S.

or γ-ray energy [*e. g.* Miss Szmidt[7], Ellis and Wooster[3], and others in connexion with the RaB/RaC γ-ray energy ratio].

The variation with frequency of the ionization per quantum is conveniently termed the "ionization function," and clearly might depend on the conditions used, *e. g.* on the shape, size, and material of the chamber, on the gas contained, on the relative positions of the source and chamber, etc.

Ionization measurements of γ-rays may be divided into two main classes: (*a*) the comparison of sources having the same spectral distribution of γ-rays, as in measurements of standards and of decay periods; and (*b*) the comparison of γ-rays of different qualities; this includes the standardization of thorium, and other, sources in terms of radium, *e. g.*[8], and also all absorption measurements, as the frequency distribution must be altered by absorption. Measurements of class (*a*) cannot be affected by the conditions used, but those of class (*b*) may be so affected. The simplest case to consider is that of the comparison of two homogeneous γ-ray beams, and this can easily be extended to more complex cases; what we can actually measure are J_1, J_2, the ionizations produced by N_1, N_2 quanta respectively of the two beams; if I_1, I_2 are the values of the ionization function of the electroscope for the two frequencies of the γ-rays, then $J_1 = N_1 I_1$, $J_2 = N_2 I_2$. If we keep the external conditions unaltered, the relative number of quanta will be unaltered, *i. e.* $\frac{N_1}{N_2}$ is constant; so $\frac{J_1}{J_2} \propto \frac{I_1}{I_2}$, and hence we can investigate the change in $\frac{I_1}{I_2}$, the ratio of the values of the ionization function for two frequencies.

2. *Objects and Nature of Experiments.*

The objects of the experiments carried out were to demonstrate as simply and unambiguously as possible the effect of the ionization function on γ-ray measurements, to obtain an idea of the magnitude and to see how it must influence past and future γ-ray ionization work. The source used was a radium standard of 7·65 mgm. giving γ-rays almost entirely from RaB and RaC; this is particularly suitable as there are two distinct groups of γ-rays, from RaB and RaC respectively, of considerable frequency

difference, while each group is itself heterogeneous. Thus, if we can measure the relative ionizations of the two groups, or of two parts of the same group, we should expect the results to be dependent on the conditions if the ionization function has any appreciable effect. For measuring the ionizations a gold-leaf electroscope of a normal type was used, the leaf being suspended inside the chamber investigated.

To vary the relative intensities of rays of different frequencies in the beam, absorption in lead sheets up to 3 cm. in thickness was used ; the results can be plotted as the logarithm of the ionization against the thickness of absorber. It was found, as is well known, *e.g.* [9], that beyond about 1·8 cm. the points lie well on a straight line, *i. e.* that the absorption is exponential. The slope of the line gives the absorption coefficient of the RaC rays, and the intercept on the axis of zero absorption gives, *vide* [7], the fractions of the total ionization due to the RaB and RaC γ-rays. For the complete description of the absorption curve, it is necessary to find also the absorption coefficient of the RaB rays by subtracting the effect of the RaC rays.

It is not possible to make use of a change in ionization function due to altering the shape or size of the chamber or the relative positions of source and chamber, for, as has been pointed out by Keetman [10] and others, the absorption curves are here altered owing to differences in the γ-rays entering the chamber, because of scattering. We are here concerned with the difference in the effects of similar beams of γ-rays, so we must keep all conditions outside the chamber constant. The changes in conditions that remain available are alterations of the gas or pressure inside the electroscope, and change of lining of the electroscope. The first experiments carried out were concerned with the effect of pressures above atmospheric; but, to an accuracy of about 4 per cent. in relative ionizations, the absorption curves showed no definite alteration for pressures up to $2\frac{1}{2}$ atmospheres, so description of the experimental arrangement is needless. The variation of the gas in the chamber was carried out in one instance by using CO_2 in place of air, and the effect was inappreciable ; but there are considerable features of interest in other work on the subject ; Rutherford and Richardson [11] and Richardson [12] used methyl iodide in the chamber, and increased the effect of the RaB γ-rays to 85 per cent. of the total effect, as compared with 10–20 per cent. for air ; they also noticed that the absorption coefficient for the RaC rays is different

with methyl iodide from that with air ; these results will be considered later together with the results of the present experiments. The alteration of lining was next investigated, and lead and aluminium were used ; eight different arrangements could be obtained by changing the base, walls, and top. Work on the variation of lining has previously been carried out by Bragg [4], Keetman [10], Sutherland and Clark [13], and others ; Bragg and Keetman found variation, with the γ-rays used, of the relative ionizations for different linings ; Sutherland and Clark found variation with the position of the source ; and Keetman made some measurements of absorption curves, in which he found the soft rays more effective with a lead lining than with zinc or paper linings. These results will also receive further consideration.

3. *Experimental Arrangements.*

Owing to the great effect of the particular geometrical form of the apparatus used, this must be described in some detail, and its general form can be best seen from the diagram (fig. 1).

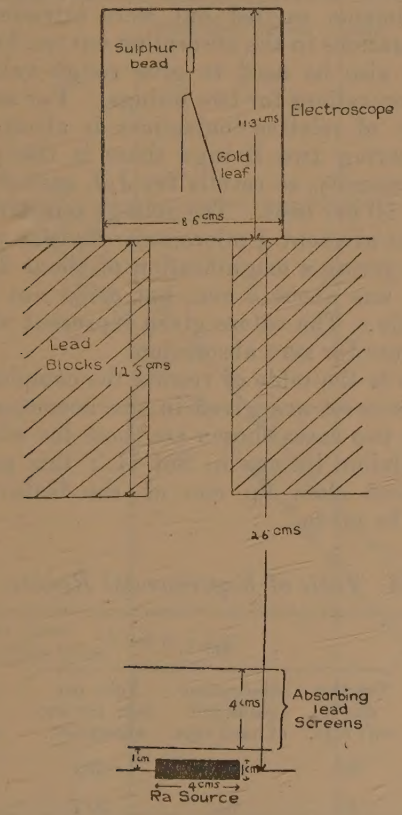
The electroscope was a cylindrical brass vessel with axis vertical ; the base was 4 mm. thick and the walls 2 mm. The electroscope was covered with 2–3 mm. of lead to exclude stray scattered γ-rays, which were further decreased by the position of the electroscope in front of a glass window. The lead linings were 1·53 mm. thick, the aluminium lid and base linings 1·63 mm., and the wall linings 3·26 mm. To change the linings the lid was completely removed.

The lead blocks enclosed a rectangle about $2\frac{1}{2} \times 5$ cm. ; the absorbing screens were rectangular, and all within the limits of 10×8 cm.^{2} and 6×6 cm.^{2}; the source was cylindrical, of diameter about 1 cm. and length about 4 cm. The geometry of the apparatus was so arranged that the only γ-rays able to impinge on the side walls were those scattered in the base ; this obviously is the best arrangement for theoretical discussion, but the canalization, necessary to ensure this result, reduces the intensity considerably, and would not in general be desirable. To ascertain the effect of allowing the γ-rays to hit the sides of the chamber, another set of experiments, referred to as Set II., was carried out, when the distance from the source to the base of the electroscope was 18 cm., the thickness of the lead blocks 4 cm., and the square enclosed of side about $4\frac{1}{2}$ cm. Set II. represents more nearly the

disposition of the apparatus in the normal use of a γ-ray electroscope. Other conditions were similar in the two sets.

The sensitivity of the electroscope did not remain quite constant, and so readings were taken with a standard absorber [1·69 mm. of lead] between readings with other absorbers; each group between standards contained cases

Fig. 1.



of large and small absorption intermingled, to eliminate systematic changes.

Readings were corrected in the usual way for natural leak, and the results represented by plotting log I/I_0 against absorbing thickness, where I_0 is the corrected rate of leak for the standard absorber, obtained, for the time when I was measured, by interpolation between the two standard readings.

The best straight line on the logarithmic curve, for points beyond 1·8 cm. absorption, is drawn, and from the slope and intercept we can obtain the absorption coefficient and fraction of ionization due to soft rays. Since the drawing of the best line is subject to some errors, no very great accuracy can be claimed for the results, and there may be 3–4 per cent. error in the absorption coefficients and 10–15 per cent. error in the fraction due to soft rays.

The experiments carried out were intended mainly to show the alterations in the absorption curves, but the results obtained can also be used to give rough values of J/J', the relative ionizations for two linings. For any one lining the accuracy of relative ionizations is about 1 per cent., but in comparing two linings there is the possibility of a change in capacity, so results for J/J_1 cannot be relied on to more than 10 per cent. The voltage sensitivity remained fairly constant at about $\frac{1}{3}$ micrometer division per volt, with a microscope giving a magnification of about 20 diameters; the capacity was about 5 cm., but could not be measured very accurately. The values given represent the current in volts per minute for zero absorption.

In addition to the table of results the complete absorption curves for two cases are given in the accompanying graph (fig. 2). The two cases chosen are those for wholly lead and wholly aluminium linings in Set II.; this pair is chosen since they best show up one of the features of which mention will be made.

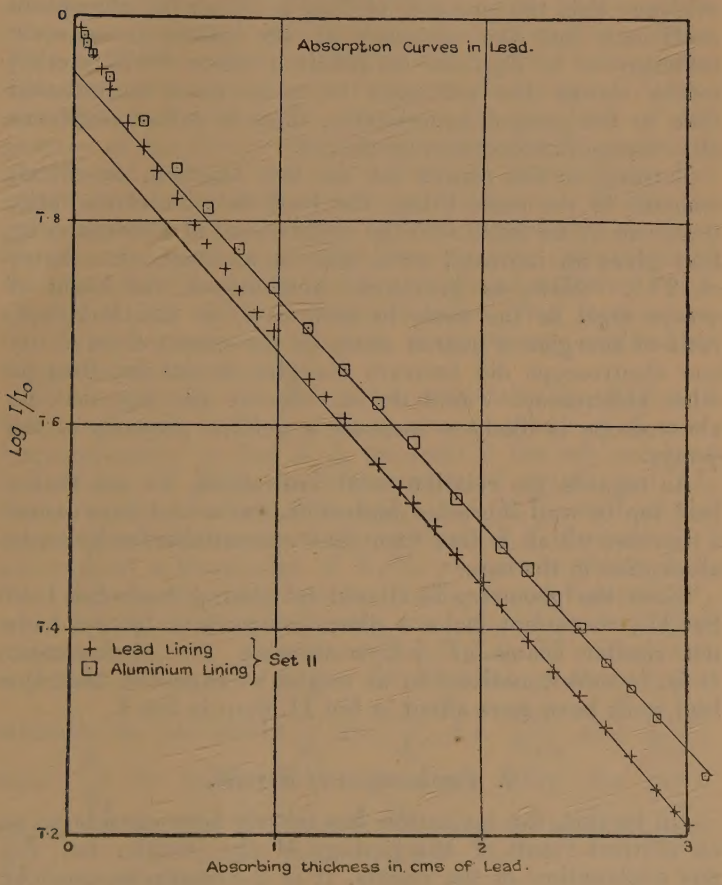
4. *Table of Experimental Results.*

Conditions.			Set I.			Set II.	
Base.	Walls.	Top.	Fraction due to soft rays.	Absorption coefficient of hard rays.	Volts per min. for zero absorption.	Fraction due to soft rays.	Absorption coefficient of hard rays.
←—	Pb	—→	·25	·50	43·4	·185	·54
←—	Al	—→	·12	·51	20·7	·06	·52
Pb	←— Al —→		·19	·51	19·8	·20	·51
Al	Pb	Al	·19	·51	43·2	·265	·50
←—Pb —→		Al	·22	·50	36·5	·22	·53
Al	←— Pb —→		·20	·52	53·4	·26	·52
←— Al —→		Pb	·20	·50	28·6	·16	·52
Pb	Al	Pb	·26	·49	27·2	·19	·52

5. *Discussion of Experimental Results.*

It is at once obvious from the table, and, perhaps, more obvious from the graph, that the absorption curves are very materially altered by changing the lining. It must be

Fig. 2.



emphasized that all conditions, except the lining, are kept identical throughout one set. Although we may not be able to define what γ-rays actually are entering the electroscope, we can be confident that for any one absorption, in one set, the same beam of γ-rays enters the electroscope no

matter what may be the lining; no correction has been made for absorption of γ-rays in the base, which is thicker than the maximum range of the secondary β-rays; such a correction would tend to accentuate the differences noticed between absorption curves for different linings.

Considering first the values of the absorption coefficient, there does appear in Set II., though not in Set I., to be some evidence that the presence of lead increases the absorption coefficient, but the accuracy of the values is scarcely sufficient to be regarded as definite; where [11], [12] methyl iodide causes the soft rays to to be more accentuated than in the present experiments, there is definite evidence of a change in absorption coefficient.

Turning to the results for the soft fraction, or, which amounts to the same thing, the RaB/RaC ionization ratio, there can be no doubt that the replacement of aluminium by lead gives an increase, which may be as much as a factor of 2:1. Now, as previously emphasized, the beam of γ-rays must be the same in each case, so the RaB/RaC ratio of energies or quanta must be the same; thus, if any one electroscope did measure energies or quanta, then no other electroscope would do so. So we can say that no electroscope is likely to measure a definite property of the γ-rays.

As regards the relative total ionizations, we see that a lead top or wall increases ionization, but a lead base causes a decrease which is less than that accountable for by extra absorption in the base.

Since the geometry is altered in passing from Set I. to Set II., we cannot make a direct comparison, for we have not similar beams of γ-rays entering the electroscope. It is, however, noticeable, as might be expected, that the lead walls have more effect in Set II. than in Set I.

6. *Explanation of Results.*

Up to this, the ionization has merely been considered as an indirect result of the passage of the γ-rays; but, for any explanation of the results, it is necessary to consider in some detail the various processes involved between the passage of the primary γ-rays and the ionization produced. The γ-rays may be absorbed photo-electrically or scattered according to the Compton effect, in the metal or in the gas, and will in each case give rise to a secondary β-ray; the β-rays produced in the metal may emerge into the gas,

the chance of so doing depending on their place of origin, energy, and direction of emission, and on their chance of absorption before emergence. The β-rays, when travelling in the gas, will lose energy which appears as ionization, the amount depending on the velocity of the β-rays; when they strike the walls of the electroscope the β-rays may be absorbed or they may be scattered back [reflected], the chance depending on their velocity. Also, γ-rays which have been scattered will possibly again give β-rays later. For a complete analysis of the problem it would be necessary to use: (*a*) the laws of scattering and absorption of X-rays and their conversion into β-rays; (*b*) the laws of the passage of the β-rays through matter, including scattering and loss of energy; and (*c*) the relation of the energy lost by β-rays in a gas to the ionization produced. Besides the great amount of calculation involved, there are so many features of uncertainty in the laws that the calculation of the ionization function is not, at present, practicable; rough approximations will be considered later. But, fortunately, the main features can be given a qualitative explanation without such calculations.

To simplify the discussion, we must take the RaB and RaC rays each to form a homogeneous group of X-rays. Experimentally we find J_1/J_2 the ratio of the soft and hard ionizations; if N_1N_2 are the number of quanta and I_1I_2 the ionization functions, then $J_1/J_2=N_1I_1/N_2I_2$; without the calculations mentioned we cannot obtain I_1/I_2 theoretically, and without a knowledge of N_1/N_2 we cannot obtain I_1/I_2 from experiment. All data for N_1/N_2, except Kovarik's [2], which is only obtained indirectly, are derived from ionization measurements, *i.e.* depend on N_1I_1/N_2I_2. If primed and unprimed letters refer to two different linings, then experimentally we can obtain $\frac{J_1}{J_2}$ and $\frac{J_1'}{J_2'}$, *i.e.* $\frac{N_1I_1}{N_2I_2}$ and $\frac{N_1I_1'}{N_2I_2'}$, since $\frac{N_1}{N_2}$ is unaltered, the geometry being the same. Hence we can get $\frac{J_1}{J_2}\Big/\frac{J_1'}{J_2'}=\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'}$, and no knowledge of $\frac{N_1}{N_2}$ is now needed.

We are now in a position to consider the explanations advanced by previous workers, in particular Bragg [4] and Keetman [10]. Bragg's work is concerned with different linings, without alteration of the quality of the γ-rays, *i.e.* he is concerned only with the variation with lining of

the ionization function for one beam, not, as in the present experiments, with the change of the relative values for two beams. His theory is that the ionization is proportional to: (*a*) the mass absorption coefficient of the lining, and (*b*) the total range in the lining of the secondary β-rays. We shall see that other factors are also concerned, but Bragg's theory contains the most important features. Keetman measured the relative ionizations in lead- and paper-lined chambers for γ-rays from Ra(B+C), MsTh and RdTh in each case filtered and unfiltered; by considering the ionization to depend only on the chances of absorption in the gas and metal, he obtains an explanation which, though incomplete, is adequate to account for his experimental results.

To account for the experimental results, we must compare, in turn, pairs of conditions where one part alone of the lining is altered from aluminium to lead. As above, if suffices 1 and 2 refer to soft and hard rays, and the primed and unprimed symbols to the two lining conditions, we find experimentally the ratio $\frac{J_1}{J_2}\Big/\frac{J_1'}{J_2'}$, where J's represent ionizations. This, we have seen, is equal to $\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'}$, where I's represent the ionization functions. Since the ionization is due to the secondary β-rays, and these can have different origins, we must divide each I into four parts, A, B, C, and D, corresponding to photo-electric effect and Compton effect in the metal, and the two effects in the gas respectively.

$$\text{So } \frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'} = \frac{A_1+B_1+C_1+D_1}{A_2+B_2+C_2+D_2} \times \frac{A_2'+B_2'+C_2'+D_2'}{A_1'+B_1'+C_1'+D_1'}$$

We know theoretically [14] that for γ-rays the chance of photo-electric effect varies with wave-length according to a power between 2·5 and 3, and Ahmad [5] has shown variation with the 4th power of Z, the atomic number. We can use approximately an extrapolation of the $\lambda_0 Z^4$ law [15], valid for X-rays, and compare this with the law for the Compton effect [16], [17], where variation with wave-length is small, and with Z of the first power. Thus we see that photo-electric effect is negligible for air and aluminium, compared with the Compton effect, but of the same order for lead; this is verified by Ahmad's [5] separation of the effects proportioned to Z and to Z^4. So, with air in the electroscope, we may neglect the "C" terms, while for a lining wholly of aluminium we may also neglect the "A" terms.

As the simplest case for detailed consideration, we will take the replacement of an aluminium base lining by one of lead, the rest of the lining being taken, for definitiveness, to be aluminium, though the arguments apply equally to the other cases. If the unprimed and primed symbols refer to the aluminium and lead base linings respectively, and the suffices 1 and 2 to the RaB and RaC γ-rays, then the measured RaB/RaC ratios give, as we have seen, a value for $\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'}$, where I's are ionization functions or ionizations per quantum. In Set I. this is, in the case considered, equal to ·4 approximately, and we have to account for this. Since the lead base absorbs the γ-rays more than does the aluminium base, and this is more effective for the soft rays, this alone would make $\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'}$ equal to about 1·3*. So the remaining effect, accountable for by the partition of I into A, B, C, D, must give, if acting alone, a value for $\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'}$ of $\frac{\cdot 4}{1\cdot 3} = \cdot 3$, and we must account for this value, if I's are now ionizations per quantum reaching the top of the base lining. The ionizations due to Compton absorption in the gas and top [and also in the walls when the argument is extended to Set II.] will be unaffected by the change of base lining; so, including the effect from the top lining with that from the gas, $D_1 = D_1'$, $D_2 = D_2'$. It can be shown that the ratio of ionizations due to Compton effect in the base for the two γ-rays is the same for both linings, *i. e.* $\frac{B_1}{B_2} = \frac{B_1'}{B_2'}$, but this is considerably less than the ratio for

* Using priming and suffices as before, let $\mu_1\mu_2\,\mu_1'\mu_2'$ be absorption coefficients, x, x' the thicknesses of the base lining, and N_1N_2 the numbers of quanta at the under side of the base lining. Then the numbers of quanta at the upper side of the base lining will be: $N_1e^{-\mu_1 x}$, $N_2e^{-\mu_2 x}$, $N_1e^{-\mu_1' x'}$, $N_2e^{-\mu_2' x'}$. If this alone affected $\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'}$, it would give a value of

$$\frac{e^{-\mu_1 x}}{e^{-\mu_2 x}}\Big/\frac{e^{-\mu_1' x'}}{e^{-\mu_2' x'}} = e^{(\mu_1'-\mu_2')x' - (\mu_1-\mu_2)x}.$$

Using the values

$\mu_1 = \cdot 57$ cm.$^{-1}$, $\mu_2 = \cdot 13$ cm.$^{-1}$, $\mu_1' = 2\cdot 9$ cm.$^{-1}$, $\mu_2' = \cdot 51$ cm.$^{-1}$,
$x = \cdot 163$ cm., $x' = \cdot 153$ cm.,

this gives

$$e^{2\cdot 4\times 1\cdot 53 - \cdot 44\times 1\cdot 63} = e^{\cdot 29} \text{ approximately} = 1\cdot 3.$$

photo-electric effect, $\frac{A_1'}{A_2'}$*. This shows certainly that $\frac{I_1}{I_2}/\frac{I_1'}{I_2'}$ will be less than 1, and we can obtain the expected

* Neglecting the change of γ-ray intensity in the β-ray range [though this can be brought in by altering "f" later], the base lining may be considered to be a homogeneous though non-isotropic source of Compton secondary β-rays. For any given γ-ray the energy of the β-ray ejected at any angle is independent of the metal. Experiments have been carried out by W. Wilson [18], Varder [19], Madgwick [20], and others on the ionization due to homogeneous β-rays after passage through various thicknesses of absorber, using different metals and β-ray velocities; the resulting curves cannot be directly used, for they depend on the electroscope used, but they show two general results of considerable use: (*a*) the "range" of the β-rays, in electrons per sq. cm., is nearly the same for all metals for one β-ray velocity; (*b*) the form of the curve is nearly the same with change of abscissal scale, for one metal for all velocities; that is to say, the area under the curve is equal to the product of the ionization for zero absorption, the range, and a factor "f" which depends only on the metal and not on the velocity.

Since β-rays are produced at all distances under the surface, the total ionization due to β-rays ejected at angles from θ to $\theta+\theta d$ will be this area mentioned; this is $f \,.\, k\,d\theta \,.\, i \,.\, \mathrm{R}\cos\theta$, where $k\,d\theta$ is the chance in unit distance [1 electron per sq. cm.] of one quantum causing the ejection of a β-ray at this angle, i the ionization produced by one such β-ray ejected at the surface, and R the range [in electrons per sq. cm.] [k, i, and R all depend on θ, but the suffix is omitted]. Using lead in place of aluminium, k, i, and R are unaltered, depending only on the Compton effect, which is an electronic, not atomic, property; so the ratio of ionizations will be f/f'. Integrating for all angles, we get

$$B_1/B_1' = f/f'. \quad \text{Similarly } B_2/B_2' = f/f'. \quad \text{Thus} \frac{B_1}{B_2} = \frac{B_1'}{B_2'}.$$

Now, turning to the "A'" terms, we can use priming to refer to photo-electric effect, for the Compton effect is the same for the two linings, except for "f's." If E_1, E_2 are the energies of Compton electrons at θ for γ-rays of frequencies $\nu_1\nu_2$, we have [21]: $E_1/E_2=(\nu_1/\nu_2)^n$, where $1<n<2$. If E_1', E_2' are photo-electric energies, $E_1'/E_2' = \nu_1/\nu_2$. If we assume that $Ri\cos\theta \propto \nu^m$, then

$$R_1 i_1 \cos\theta/R_2 i_2 \cos\theta = (\nu_1/\nu_2)^{mn} \quad \text{and} \quad R_1' i_1' \cos\theta/R_2' i_2' \cos\theta = (\nu_1/\nu_2)^m$$

Hence

$$B_1/B_2 = (\nu_1/\nu_2)^{mn} \,.\, \sigma_1/\sigma_2,$$

where σ_1, σ_2 are Compton absorption coefficients, and

$$\sigma_1/\sigma_2 = (\nu_1/\nu_2)^p,$$

where $-1<p<0$. But

$$A_1'/A_2' = (\nu_1/\nu_2)^m \,.\, r_1/r_2,$$

where r_1, r_2 are photo-electric absorption coefficients, and

$$r_1/r_2 = (\nu_1/\nu_2)^r,$$

where $-3<r<-2{\cdot}5$ [14]. So

$$\frac{A_1'}{A_2'}/\frac{B_1'}{B_2'} = \left(\frac{\nu_1}{\nu_2}\right)^{m+r}/\left(\frac{\nu_1}{\nu_2}\right)^{mn+p} = (\nu_1/\nu_2)^{m(1-n)+r-p}.$$

value of ·3 by a rough calculation * of the relative magnitudes of the ionizations from different sources; since considerable approximations have been made, as much reliance cannot be placed on this agreement as might at first be expected, but it does show that the relative magnitudes are not far wrong. The same argument can be applied to all cases of the replacement of the aluminium base by lead, and a very similar effect is shown in the replacement of the aluminium top lining by one of lead; since the Compton electrons are all ejected forward, those emerging from the top lining must have been scattered back, and so it is not possible to apply this preceding

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Now $1-n$ and r are negative, p is $<-r$, so we can deduce that $A_1'/A_2 > B_1'/B_2'$.

If β is the β-ray velocity, then, neglecting high-order terms in β, $E \propto \beta^4$ and i for unit distance $\propto \beta^{-2}$; we can say that i probably $\propto \beta^s$, where $-3<s<-1$. So $Ri\cos\theta \propto \beta^{4+s}$ or $\propto E^{2+2\frac{1}{2}s}$. Thus $m = 2+\frac{1}{2}s$.

So
$$\frac{A_1'}{A_2'} \Big/ \frac{B_1'}{B_2'} = \left(\frac{\nu_1}{\nu_2}\right)^{(2+\frac{1}{2}s)(1-n)+r-p} = \left(\frac{\nu_1}{\nu_2}\right)^t,$$

where the outside limits for t are $-5\frac{1}{2}<t<-2\frac{1}{2}$. But $\nu_1/\nu_2 =$ approx. $\frac{1}{3}$, so we get

$$3^{5\frac{1}{2}} > \frac{A_1'}{A_2'} \Big/ \frac{B_1'}{B_2'} > 3^{2\frac{1}{2}} \quad \text{or} \quad 500 > \frac{A_1'}{A_2'} \Big/ \frac{B_1'}{B_2'} > 15.$$

* The mean energy of the Compton electrons can be found from the theoretical values [21] of the numbers and total energies of the Compton electrons; if a is the value of $\cdot 024/\lambda$ [λ in Å], the mean energy E is $\frac{a^2}{1+2a} m_0c^2$. For the RaC rays, $a = 1{\cdot}5$ nearly, so $E_2 = \frac{(1{\cdot}5)^2}{4} m_0c^2$, while E_2', the energy of the photo-electron, is am_0c^2; thus $E_2/E_2' = {\cdot}375$; then, as before,

$$R_2 i_2 \cos\theta / R_2' i_2' \cos\theta = (E_2/E_2')^m,$$

where $\frac{1}{2} < m < 1\frac{1}{2}$, giving $\cdot 23 < R_2 i_2 \cos\theta / R_2' i_2' \cos\theta < {\cdot}61$. Using Ahmad's [5] values of σ_2, τ_2 per atom of lead as $13{\cdot}8\times10^{-24}$ and $7{\cdot}2\times10^{-24}$ respectively, $\cdot 44 < B_2'/A_2' < 1{\cdot}16$.

$B_2 = ki_2R_2\cos\theta . f$; $D = ki_2 d$, where d is the height of the electroscope in electrons per sq. cm. Thus $B_2/D_2 = R_2\cos\theta f/d$; similarly $B_1/D_1 = R_1\cos\theta f/d$. So

$$\frac{B_1}{B_2} \Big/ \frac{D_1}{D_2} = \frac{R_1}{R_2} = (E_1/E_2)^2 \doteq (\nu_1/\nu_2)^{2n},$$

where $1<n<2$. There is, in addition, the part of the ionization due to Compton effect in the top; hitherto we have considered this with D, but it must now be treated apart. This effect can only be due to Compton electrons scattered back; we know [22, 23] that reflexion at aluminium gives about 30 per cent. of the initial ionizing power, but the rays are less penetrating, so R is less. We will take this as approximately $\frac{1}{5}$B. From Varder's [19] ranges we can get R for electrons of the mean energy

analysis directly. For the change of wall lining from aluminium to lead there are two opposing effects; first, there is that of γ-rays scattered from the base; here, in the same way as for the base, the presence of lead increases the RaB/RaC ratio. On the other hand, there is an effect due to reflexion of β-rays at the walls; it is known [22, 23] that β-rays are more readily reflected by lead than by aluminium; the faster the β-ray the greater is the energy loss on reflexion, and hence the greater the loss of ionizing power, for the fraction reflected varies slowly with velocity; since more energy is lost by β-rays from the hard γ-rays and more energy is lost at aluminium walls, we see that this would give a decrease in the RaB/RaC ratio when lead replaces aluminium for the wall lining. The two opposing effects give in some cases an increase and in some a decrease of the ratio.

We have seen how the general results for the RaB/RaC ratio can be explained qualitatively for Set I.; similar considerations can be applied to Set II., bearing in mind that the γ-rays from the source are falling directly on the walls. The absorption coefficients can be dealt with similarly, most simply by considering two groups of RaC γ-rays; then we should expect to find a higher absorption coefficient where there is a higher RaB/RaC ratio. This is not noticeable in Set I., but may be found in Set II.; but, if there is a small inaccuracy in drawing the line, this will, at the same time, increase the RaB/RaC ratio and decrease the absorption coefficient, or *vice versâ*. The definite change of absorption coefficient in the work of Rutherford and Richardson [11] with methyl iodide is explained by photo-electric effect in the gas, *i. e.* by the "C" terms here negligible.

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of the Compton electrons, and, using for θ the angle corresponding to the mean energy, we get $B_2/D_2 = 3f$ approximately. In order to make calculations, we use

$$\frac{A_1'}{A_2'}\Big/\frac{B_1'}{B_2'} = 100, \quad \frac{B_2'}{A_2'} = 1, \quad \frac{B_1}{B_2}\Big/\frac{D_1}{D_2} = \frac{1}{30}, \quad f = \tfrac{1}{2}, \quad \text{and} \quad f' = \tfrac{1}{3}.$$

Then

$$\frac{I_1}{I_2}\Big/\frac{I_1'}{I_2'} = \frac{B_1+D_1}{B_2+D_2}\Big/\frac{A_1'+B_1'+D_1'}{A_2'+B_2'+D_2'}$$

$$= \frac{B_1+B_1\times\dfrac{30}{3\times\frac{1}{2}}+\dfrac{B_1}{5}}{B_2+\dfrac{B_2}{3\times\frac{1}{2}}+\dfrac{B_2}{5}}\Big/\frac{100B_1'+B_1'+B_1'\times\dfrac{30}{3\times\frac{1}{3}}+\dfrac{B_1'}{5}}{B_2'+B_2'+\dfrac{B_2'}{3\times\frac{1}{3}}+\dfrac{B_2'}{5}}$$

$$= \frac{1+20+\frac{1}{5}}{1+\frac{2}{3}+\frac{1}{5}}\Big/\frac{100+1+30+\frac{1}{5}}{1+1+1+\frac{1}{5}} = \cdot 3 \text{ approximately.}$$

Turning to the results for relative intensities in the two electroscopes, these can also roughly be explained *, though the agreement is only to 20 per cent. ; bearing in mind the difficulty in connexion with the capacity, this is quite satisfactory.

It is possible to use the same approximations, as have given the above agreement with experiment, to obtain a value of the RaB/RaC energy ratio ; this gives a value of about ·10 †, in good agreement with accepted values, *e.g.*[3] ; this might make it appear desirable to carry out the calculations in more detail, but at present there is so much margin of doubt in the fundamental laws used that we must wait until further experimental data can give the laws more definitely. Though the approximations used are very rough, they give a satisfactory explanation of other results, and so may justifiably be applied to the calculation of the RaB/RaC ratio.

7. *Electroscope Measurements.*

As suggested by the arguments in the introduction, γ-ray ionization measurements are very considerably influenced by the ionization function. Ionization measurements, particularly with electroscopes, are exceedingly convenient for γ-ray work, but electroscopes can only measure ionizations, and we have seen the difficulty of correlating ionizations with definite properties of the beam. By considering various types of γ-ray measurements, we will illustrate the uses and limitations of the electroscope.

An interesting type of measurement to consider is that of the comparison of radium and thorium standards by means of γ-rays ; since the γ-rays are of different hardness, it has long been recognized that the comparison must depend on the amount of filtration, and comparisons are always given as measured through a certain thickness of lead ; but, since the

* For hard rays in the wholly aluminium electroscope, the ionization is $\cdot 88 \times 20 \cdot 7$ volts/minute ; with a lead base, it is $\cdot 81 \times 19 \cdot 8$. This gives a ratio experimentally of $18 \cdot 2/16 \cdot 0 = 1 \cdot 14$. In the preceding calculations, $I_2/I_2' = \frac{28}{15} B_2/\frac{16}{5} B_2'$, but $B_2/B_2' = f/f' = 3/2$; so $I_2/I_2' = 7/8$; correcting for absorption in the base, this gives $\cdot 68/\cdot 74 = \cdot 92$.

† For a wholly aluminium electroscope, $N_1 I_1/N_2 I_2 = \cdot 12/\cdot 88$ experimentally. From the previous calculations, $I_1/I_2 = \frac{106}{5} B_1/\frac{28}{15} B_2$ and $B_1/B_2 = (\nu_1/\nu_2)^{mn+p}$. With the same kind of approximations as before, $B_1/B_2 = \frac{1}{25}$. Whence we get $I_1/I_2 : \cdot 452$; so $N_1/N_2 = \cdot 30$ and $E_1/E_2 = \cdot 10$.

γ-rays are of different qualities, the electroscope used will have an effect, and so a comparison of γ-ray activities of radium and thorium sources should include a specification of the electroscope used, as well as of the thickness of lead. An important determination of this type is the ratio of the number of α-particles from radium and thorium when the γ-ray activities, measured through a certain thickness of lead, are equal; this has been carried out by Shenstone and Schlundt [8], and by Watson and Henderson [24], but their results are not absolute, depending as they do on the electroscope used; but, since Watson and Henderson required their results for work on the heating effect of α-rays [25], and they used the same electroscope for the purpose of measuring the strengths of sources in the two experiments, so they are justified in using the results. Any other property of the sources would have been equally useful, but the γ-ray ionization is most convenient. This forms a good example of the way in which ionization measurements may be applied without error, even though they are concerned with γ-rays of different qualities.

As seen from the present experiments, and from previous work on the subject, the RaB/RaC ratio depends very largely on the electroscope used. It also appears probable that absorption coefficients are similarly affected; since absorption coefficients are made the basis of much theoretical work, *e. g.* [5], [6], [26], it is useful here to consider them more fully; if we can measure quanta, N, or energies, E, as well as ionizations, J, we can obtain the three absorption coefficients μ_N, μ_E, and μ_J, from $N = N_0 e^{-\mu x}$ etc. With a homogeneous beam of γ-rays, μ_N, μ_E, and μ_J would be equal, but no such beam can be obtained, and if obtained would soon become heterogeneous by scattering; thus μ_J can never be equal to μ or μ_E, and this is the reason why absorption coefficients for ionizations cannot be used to give energy values, *e. g.* [3].

The most interesting of the deductions from absorption coefficients is that of Kohlrausch [6]. Using γ-ray intensities deduced from Thibaud's [27] results, and the accepted absorption laws [15], [16], he calculates the expected absorption coefficients, and finds divergences from those from ionization measurements; he is tacitly assuming that each quantum produces equal ionization, thereby neglecting the ionization function, but it is unlikely that this will produce sufficient effect to account for his divergences, which must still be traced to the absorption laws.

From these experiments it is also possible to obtain

information to guide in the choice of an electroscope for a particular purpose ; from the absolute values, we see that the greatest ionization is produced in an electroscope with an aluminium base and the rest of lead ; this, then, is the type to be chosen for the greatest sensitivity. If the presence of the soft rays will cause difficulties, either directly or due to such factors as transient equilibrium, then these can be minimised by the use of a wholly aluminium lining ; for β-ray measurements it is desirable to diminish the γ-ray effect, and here again the completely aluminium electroscope is desirable.

The next question of importance is to consider whether any experimental arrangement can be devised by which the effect of the ionization function can be either eliminated or rendered easily calculable. Moseley and Robinson [28] used a very thin-walled electroscope in air and assumed the ionization inside to be equal to that in an equal volume of air ; hence, knowing the absorption coefficient of air, it is possible to obtain the γ-ray energy by integrating the ionization over all space ; but their basic assumption is not justifiable exactly, and other difficulties occur. Ahmad [5] allowed the γ-rays to fall in succession on a number of parallel lead plates with air between ; if all the secondary β-rays emerge from the plates, if we can neglect loss of energy at reflexion of the β-rays, and if all the γ-rays are absorbed, then ionization will be proportional to energy, but these conditions are not fulfilled. To obtain a method which allows ionization functions to be easily calculated, we are faced with the difficulty of obtaining a definite value for the ionization due to a single secondary β-ray ; with a very large ionization chamber, or high gas-pressure, the ionization might be due to its whole energy, but here we will have difficulties due to the " D " terms, from Compton absorption in the gas. With a small chamber, or low pressure, and poorly reflecting walls we might expect the ionization to depend on 1/energy, but it is impossible completely to eliminate the effect of reflexion. So we see it is not easy to devise an electroscope suitable for direct measurement of the γ-rays. It seems that electroscope measurements, while ideal for the comparison of similar beams of γ-rays, may only be used for beams of different quality when it is realized that ionizations are the only factors measurable. When there is any question of deducing some definite property of γ-ray beams, *e.g.* energy or quanta, then ionization measurements are only in general useful for giving a very rough indication of the value (*e.g.* Aston [29]).

8. *Summary.*

The ionization produced in a chamber is only dependent on primary γ-rays through the agency of the secondary β-rays, and hence may not measure any definite property of the γ-ray beam ; experiments have been carried out which show striking alterations in the relative ionizations of the RaB and RaC γ-rays when the electroscope lining is altered, the γ-ray beam being the same. A qualitative and a very rough quantitative explanation are given, using well-known ideas of absorption and scattering of β- and γ-rays. This demonstrates the part of an "ionization function" in γ-ray measurements, and the consequences of this are considered in relation to past work and in connexion with the limitations necessary in the use of ionizations to measure γ-rays.

It is a great pleasure to thank Professor Sir Ernest Rutherford, who suggested the problem, for his interest, and Dr. C. D. Ellis, who is responsible for many of the ideas embodied in this work, for his constant help and advice.

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LXXII. *The Heartbeat considered as a Relaxation Oscillation, and an Electrical Model of the Heart.* *By* BALTH. VAN DER POL, *D.Sc., and* J. VAN DER MARK *.

[Plates X.–XII.]

1. *Relaxation Oscillations.*

THE equation

$$\ddot{v} - \alpha(1-v^2)\,\dot{v} + \omega^2 v = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is representative of an oscillatory system of which the resistance is a function of the elongation. When α is a positive quantity the system has a resistance which for a small amplitude is negative. Therefore, the position

$$v = 0$$

is unstable. When, further,

$$\alpha^2 \gg \omega^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

it is obvious that as long as

$$v^2 \ll 1,$$

the variable v will initially leave the value $v=0$ in an aperiodic way, but when later

$$v^2 > 1,$$

the resistance has changed its sign and has become positive and, therefore, v will have the tendency to go back again towards $v=0$. The possibility of (1) even with the condition (2) having still a purely periodic solution is made plausible by the above considerations, and a full description of the solutions of (1) was given by one of the present authors some years ago †.

It followed from the research mentioned that the fundamental period T_{rel} of the solution of (1) with the condition (2) is

$$T_{rel} = 1{\cdot}61\frac{\alpha}{\omega^2}.$$

* Communicated by the Authors. A more detailed account of these considerations will appear in the next issue of *L'Onde Electrique.*

† Balth. van der Pol, Phil. Mag. ii. p. 978 (1926); *Jarhb. d. dr. Tel.* (*Zs. f. Hochfreq. Technik*) xxviii. p. 178 (1926), xxix. p. 114 (1927).

If (1) is taken to represent an electrical oscillation

$$\alpha = \frac{R}{L},$$

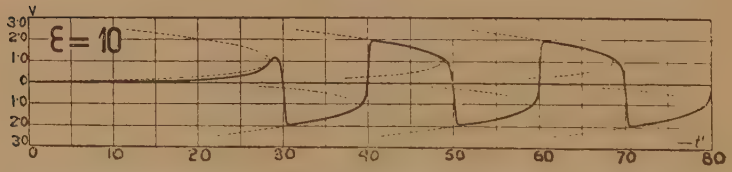
$$\omega^2 = \frac{1}{LC},$$

and thus

$$T_{rel} = 1{\cdot}61\ RC,$$

and therefore the fundamental period of the new oscillations is, apart from the numerical constant, given by a time constant or relaxation time, and for this reason the name *relaxation oscillation* was suggested. In fig. 1 (taken from the paper mentioned above) the solution of (1) is depicted, and it is seen that the "wave form" deviates very considerably from the sinus function.

Fig. 1.



Graphical representation of the solution of equation (5) with the condition $\epsilon = \alpha/\omega = 10$. In this case the equation represents a "relaxation oscillation" which is characterized *a. o.* by its form departing in a very marked way from a sinus curve. Sudden jumps are seen to occur periodically.

A further research of the behaviour of a relaxation system under the influence of an impressed periodic electromotive force of small amplitude revealed very remarkable synchronization properties *.

In fact it was found that, when this E.M.F. was near resonance, the *free* relaxation period of the system could be varied over a wide range (of the order of an octave), the system continuing to vibrate with the impressed period. Also the system was found very easily to synchronize on a *subharmonic* of the impressed E.M.F., *i. e.*, when the frequency of the latter was ω_0, the fundamental frequency of the "forced" oscillation in the system was ω_0/n, n being any whole number up to 100 or 200. These relaxation

* Balth. van der Pol and J. van der Mark, "Frequency Demultiplication," 'Nature,' Sept. 10th, 1927.

oscillations therefore enable us to realise a *frequency demultiplication*. The experiment showed that the amplitude of the relaxation oscillation could not considerably be influenced by the external E.M.F. Therefore, the frequency of a relaxation oscillation can easily be influenced by an external periodic E.M.F., while the amplitude is quite "rigid." Exactly the reverse is the case with systems obeying (1) but with the condition

$$\alpha^2 \ll \omega^2,$$

as, *e. g.*, a triode oscillator under the influence of an impressed E.M.F. *

Summarizing the properties of relaxation oscillations we have :

(*a*) their *time period* is determined by a time constant or relaxation time ;

(*b*) their *wave form* deviates considerably from a sinus, and, as very steep parts occur, many higher harmonics of pronounced amplitude are present ;

(*c*) a small impressed periodic force can easily force the relaxation system in step with it (*automatic synchronization* even on subharmonics) while under these circumstances,

(*d*) the amplitude is hardly influenced at all.

Though relaxation oscillations were originally derived in the way outlined above, it will be clear that they are to be found in many realms of nature, for there are many different types of relaxation time. We are mostly used to find a decay phenomenon to occur only once in a special experiment, and it is typical in the case of relaxation oscillations to find such an asymptotic occurrence to repeat itself periodically. Obviously this automatic periodic re-occurrence of such a typical aperiodic phenomenon is closely related to the presence of some form of energy source which is to be found behind the negativity of the resistance of (1).

Some instances of typical relaxation oscillations are : the æolian harp, a pneumatic hammer, the scratching noise of a knife on a plate, the waving of a flag in the wind, the humming noise sometimes made by a water-tap, the squeaking of a door, the multivibrator of Abraham and Bloch †, the

* This synchronisation property of a triode oscillator was first found by W. H. Eccles and J. H. Vincent, British Patent Spec. clxiii. p. 462, application date Febr. 17th, 1920. The theory of this phenomenon is to be found in Balth. van. der Pol, Phil. Mag. iii. p. 65 (1927).

† Abraham & Bloch, *Ann. de Physique*, xii. p. 237 (1919).

tetrode multivibrator *, the periodic sparks obtained from a Wimshurst machine, the Wehnelt interrupter, the intermittent discharge of a condenser through a neon tube, the periodic re-occurrence of epidemics and of economical crises, the periodic density of an even number of species of animals living together, and the one species serving as food for the other †, the sleeping of flowers, the periodic re-occurrence of showers behind a depression, the shivering from cold, menstruation, and, finally, the beating of the heart ‡.

In all these examples the frequency of these periodic phenomena is not determined by the product of an elasticity and a mass but by some form of relaxation time.

That the frequency of these periodic phenomena is not rigidly constant is due to the fact that a relaxation time is determined *a. o.* by some form of resistance, and it is a well-known fact that outer circumstances may much easier influence a resistance than a mass or elasticity.

2. *Schematic Dynamical Representation of the Heart.*

In applying the theory of relaxation oscillations to the beating of the heart we will consider the heart as a system of three degrees of freedom: the *sinus*, the *atrium* (*auricle*), and the *ventricle*. As normally the two auricles beat in exact synchronism and the same can be said of the two ventricles, we will further speak of *the* auricle and *the* ventricle.

When we consider the heart as having three degrees of freedom only, it will be obvious that we exclude at the outset those movements of the heart which can only be described by partial differential equations. For instance, we cannot find back the finite velocity of propagation of contraction over the wall of the heart. We therefore shall not consider flutter or fibrillation, as these phenomena are directly connected with progressing and standing waves.

Returning to the view of the heart having the above-mentioned three degrees of freedom only, we consider each of them to be able to perform a relaxation oscillation by itself, each of the three having its own natural period. Moreover, a coupling exists between the sinus and the auricle, the former acting on the latter. Another coupling

* Phil. Mag. li. p. 991 (1926).

† Volterra, *Accad. Lincei, Atti* (1926).

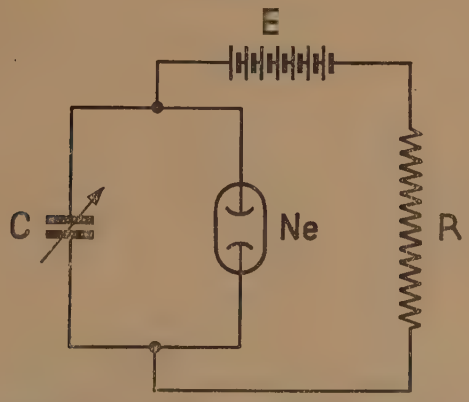
‡ The view that heart beats belong to the type of relaxation oscillations was first expressed two years ago by Balth. van der Pol (Phil. Mag. ii. p. 992 (1926)).

exists between the auricle and the ventricle, which coupling is realized through the existence of the bundle of His.

In a normal heart both the couplings mentioned have the peculiarity that they transmit a stimulus in one direction only, *i.e.*, from the sinus to the auricle, and from the auricle to the ventricle, respectively. These couplings are therefore in the normal heart of a unidirective character. In an electrical model to be described later on, these two couplings are therefore represented by two triodes, which do not amplify at all, but which were simply inserted in order to provide a unidirective instrument.

The purpose of this paper is to give a general connected view of the heartbeats considered as relaxation oscillations. The properties of these oscillations, which have lately been studied,

Fig. 2.



A system capable of producing relaxation oscillations. It consists of a neon lamp Ne, a condenser C of approximately 1 microfarad, a resistance R of the order of 1 megohm, and a battery of about 180 volt.

enable us to consider the rhythm of the heart from a new general point of view, giving a logical connected account of the heart-rhythm. According to this new theory some anomalies of the heart-rhythm can be predicted, which, so far as the authors are aware, have not yet been observed or recognized in the human heart.

3. *Electrical Model of the Heart.*

In constructing a model of the heart according to the theory expounded above, various systems capable of producing relaxation oscillations could be chosen. As a very

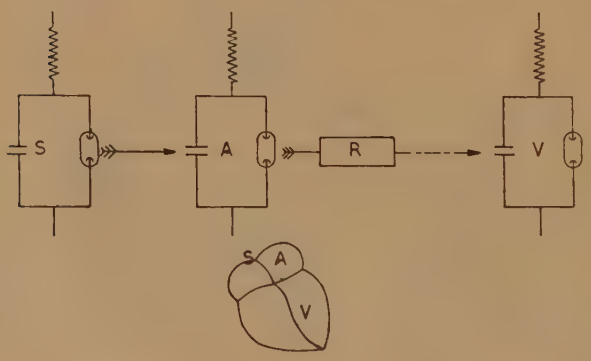
practical example, which is also well suited for demonstrations, an intermittent discharge through a neon tube can be made use of. Such a system is depicted in fig. 2, where E is a battery of say 150 to 200 volts, R a resistance of the order of 1 megohm, and C a capacity of the order of one microfarad.

As the charging-up time of the condenser is given by the product of the capacity C and the resistance R, the time period T_{rel} of this relaxation oscillation will be about

$$T_{rel} \doteqdot CR = 10^{-6} \cdot 10^{+6} = 1 \text{ sec.}$$

We therefore see the neon lamp to give a short flash once about every second.

Fig. 3.



Schematic representation of the heart by three relaxation systems: S (=Sinus), A (=Auricnlum), and V (=Ventriculum). R is a retardation system representing in the model the finite time necessary for a stimulus to be transmitted through the A-V bundle.

In fig. 3 the heart is represented by three such systems, where the first one S stands for the sinus, A for the atrium, and V for the ventricle. Between A and V a rectangle R is drawn representing a retardation system imitating the finite time taken for a stimulus to be transmitted from the atrium through the atrio-ventricular-bundle to the ventricle. In our electrical model this retardation is brought about by the action of a fourth neon tube, which therefore takes care that the ventricular systole sets in somewhat later than the corresponding auricular one. However, any other retardation system could be chosen, and we want to stress the fact that the working of our model

is independent of the type of system used for this retardation.

A photo of the complete instrument is given in fig. 4 (Pl. X.), where it is seen that the three neon tubes S, A, and V of fig. 3 are brought to the front of the instrument, each flash corresponding to the activity of the respective part of the heart.

At the back of the instrument three keys are mounted, with which a short electrical impulse can be given to the systems S, A, and V of fig. 3, thus causing extrasystolæ of the sinus, auricle, and ventricle respectively. Moreover, the coupling between A and V (the auricle and ventricle) can be varied at will, thus imitating the beautiful experiments of Erlanger of gradually clamping the bundle of His.

The whole model consists of resistances and capacities only, and no intended inductances are introduced in the system.

Electrocardiograms could be taken from this artificial heart by adding the current impulses in the auricle and

Fig. 5.

Typical electrocardiogram of the artificial heart. The P top and the QRS complex are clearly visible. The T top however is missing, due to insufficient definite data at hand as regards its origin.

in the ventricle; a further filtering circuit was used to remodel somewhat the form of the impulses, which were registered, after amplification, with a Cambridge oscillograph. Obviously this filter circuit had no influence on the working of the model, and is not used for ordinary demonstration purposes.

A typical electrocardiogram of our artificial heart, working in a normal way, is shown in fig. 5, where the P top and QRS complex is plainly visible, while the T top is missing. As the origin of the T top in the electrocardiogram of the human heart is not quite certain yet, we could not insert a representing mechanism for it.

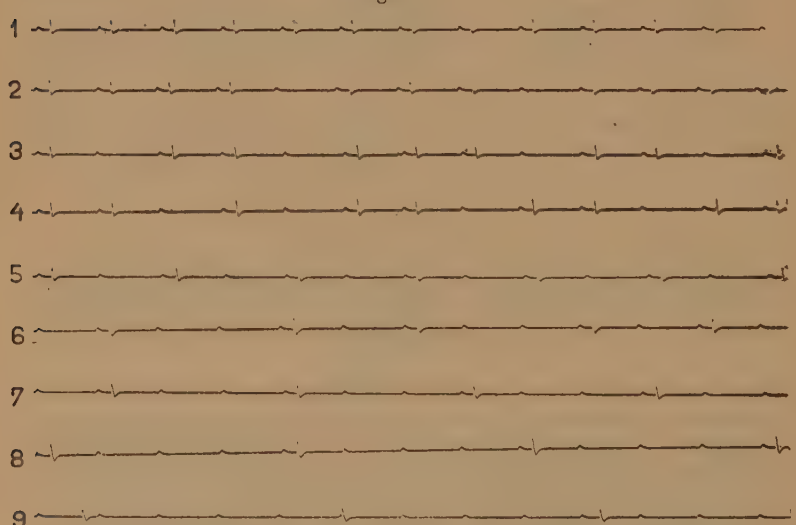
4. *Observations and Measurements made with the Electrical Model.*

4 *a*. *Heart block*.—In fig. 6 we give nine films taken with our model giving the effect of gradually decreasing the coupling between auricle and ventricle, thus imitating the experiments of Erlanger on clamping the bundle of His.

Film No. 1 gives the normal heart beat ; No. 2 shows an occasional failure of the ventricle ; in No. 3 these failures become more frequent ; in No. 4 we approach the case of 2 : 1 *heart block*, which stage is reached in film No. 5. In No. 6 we have alternatively 2 : 1 and 3 : 1 block. Further, we see in Nos. 7 and 8, respectively, 3 : 1 and 4 : 1 block, till at last in film No. 9 the coupling has become zero, which gives *complete heart block*.

A typical case of *sino-auricular block* is given in fig. 7 (Pl. X.), where the first film gives the normal heart beat and the second shows clearly the block just mentioned.

Fig. 6.



Electrocardiograms from the artificial heart obtained by gradually reducing the coupling between the A and V system (clamping the bundle of His). The development of 2 : 1, 3 : 1, and 4 : 1, as well as complete heart block, is clearly shown.

4 *b*. *Extra systolæ*.— When our heart model beats in the normal way we can impress a small electrical impulse on the ventricle. If this is done directly after a ventricular systole we find that nothing happens. The ventricle therefore is still in its *refractory period* : the condenser of the V system is not yet charged up to such a potential that the extra E.M.F., superimposed upon it causes the total potential to reach the flashing potential of the neon lamp. When we repeat the same experiment slightly later,

after a ventricular systole, we find a flash of the V system. to occur ; the ventricle has now passed its refractory state. When this flash occurs and we have therefore excited a ventricular extrasystole, the condenser discharges through its neon tube in a normal way down again to the potential where the gas discharge breaks, and thus we find back the famous law of "*all or nothing*" : a stimulus has either no effect at all or it causes a complete systole to occur. When we investigate into the magnitude of the stimulus necessary to cause a ventricular extrasystole as a function of the phase of the ventricular cycle, we find this stimulus to decrease exponentially with an increasing phase, as was to be expected. The magnitude of the stimulus E necessary to produce an extra systole as a function of the time t, counted from the moment of a former systole, is therefore represented by the formula

$$E = Ae^{-\frac{t}{CR}} - B,$$

which follows directly from the manner in which a condenser is charged through a resistance. No doubt a similar law applies to the real heart.

Consider fig. 8 (Pl. XI.), where the film No. 1 again represents the electrocardiogram of our artificial heart beating in the normal way. Film No. 2, however, shows a *ventricular extrasystole* given shortly before an impulse from the atrium arrives. It is clearly seen that the next following auricular systole finds the ventricle still in the refractory period, so that it does not cause a normal ventricular systole. When, as in No. 3, the ventricular extrasystole is caused to occur earlier in the ventricular cycle, the next coming auricular systole *does* have effect and causes the normal ventricular systole, so that here we have the case of an "*interpolated*" *ventricular systole.*

Again in fig. 9 (Pl. XI.), film 1 represents the normal working of the heart. In film 2 an *auricular extrasystole* is caused. Here, again, the auricular extrasystole is followed after the normal time by a ventricular systole, but a *compensatory period* is found after this auricular extrasystole, so that the next one comes at the normal time rigidly determined by the frequency of the sinus. Film 3 represents the same case, but with the difference that the auricular extrasystole was excited a little earlier than in film 2. Therefore the auricular extrasystole finds the ventriculum still in its refractory period, and under these

circumstances therefore the auricular extrasystole is *not followed* by a ventricular one.

Fig. 10 (Pl. XII.), No. 1, gives the normal heart beat. Film No. 2 represents a case of a *sinus extrasystole*. It is clearly seen that the original rhythm has been lost, as is the case in the human heart.

Finally, we reproduce in fig. 11 (Pl. XII.) an electrocardiogram of the human heart, taken in three normal positions 1, 2, and 3, with the same special amplifier used in the experiments with the artificial heart and also with the same Cambridge oscillograph, which has a shorter natural time period and therefore responds quicker than the string galvanometer.

This amplifier, which had the property of amplifying the very low frequencies of say one half period per second or less, as well as the higher frequencies, enabled us to make visible the real human heart beat as periodic flashes of a neon tube. This neon tube flashed twice in each heart cycle, when it was connected to the output side of the amplifier, the input side being connected to the two hands of the patient.

5. *Final Considerations and Suggestions of new Possibilities.*

The very close analogy between the working of our model and the beating of the mammalian heart leaves no doubt that the view expressed in the former paragraphs of regarding the heart beat as a relaxation oscillation is correct. Therefore, without going into the detailed nervous and physical-chemical action of the heart, it can safely be concluded that what ultimately determines the period of the heart is a *diffusion time* (a relaxation time). As mentioned above, the model described represents a first approximation only to the action of the heart, and it could be extended in several directions, thus assigning to the heart more than three degrees of freedom only.

Moreover, a reduction of the electromotive force of the battery connected to the model reduces the "tonus," and soon a point is reached where our electrical heart does not beat any more. The system under these conditions closely shows, so far as the response to an external stimulus is concerned, the behaviour of an ordinary muscle. In fact, a cross-striated *muscle* can be represented by what may be called a "*relaxation cable*," about which we hope to report in another communication.

In conclusion, we give some further possible disorders mainly obtained mathematically and which were all verified

with the aid of our model. Possibly these anomalies either have or will be found in the human heart as well.

It follows from the considerations expounded above that there are two possibilities that may cause a partial heart block :

(*a*) the amplitude of the stimulus arriving through the A–V bundle at the ventricle is smaller than normal;

(*b*) the natural relaxation period of the ventricle is prolonged.

Both causes may result in exactly the same working of the heart, though means may be found to distinguish between the two.

Fig. 12.

Transient periods elapsing after a ventricular extrasystole is given at the moment indicated by the first arrow. Only at the moment indicated by the second (dotted) arrow is the normal periodic action of the heart resumed. This figure gives the course of events calculated and verified experimentally with the aid of the model, and with the condition that the free natural relaxation period T_2 of the ventricle is larger than that (T_1) of the auricle.

But also an acceleration of the natural free ventricular period may result in anomalies, which bear some resemblance to a combination of heart block with ventricular extrasystolæ. Especially these anomalies occur when the free relaxation period of the ventricle is slightly greater or slightly smaller than the period of the sinus and when the conduction through the A–V bundle is reduced. Let, *e.g.*, fig. 12

represent the auricular and ventricular systolæ. The shaded portions following the ventricular systolæ represent the duration of the refractory period as determined *a.o.* by the amplitude of the stimulus arriving from the A–V bundle. Calling:

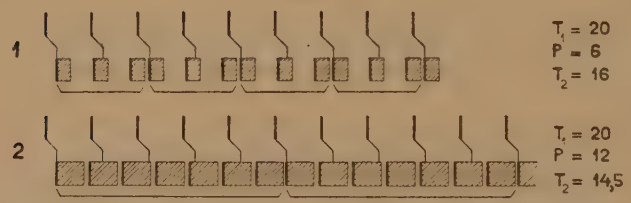
T_1 = period of the stimulus arriving from the A–V bundle.

T_2 = free relaxation period of the ventricle.

P = length refractory period.

Fig. 12, Nos. 1, 2, 3, and 4 represent different effects of extrasystolæ. The durations of T_1, T_2, and P are given at the side of the figures in arbitrary units. In this fig. 12 $T_1 < T_2$. Under these circumstances a ventricular extrasystole may temporarily disturb the rhythm (mathematically: transients). The extrasystole is everywhere indicated by

Fig. 13.



Some possibilities (derived theoretically and verified with the aid of the model) when the free natural relaxation period T_2 of the ventricle is slightly smaller than the auricle period T_1. The shaded portions indicate (like in fig. 12) the refractory period of the ventricle. Especially No. 1 shows the possibility that the fundamental period of the rhythm in this case is *not* equal to the period of the auricle, but is twice as long. Here *three* ventricular systolæ occur in the time of only *two* auricular systole. The last ventricular systole in each fundamental period resembles somewhat to cause a retrograde beat of the auricle.

an arrow, while the dotted arrows give the beginning of normal working of the heart again. The anomalies of figs. 12 and 13 have been derived on the basis of a strict unidirectional conduction through the A–V bundle, and it will be clear from these figures that some of the anomalies resemble somewhat "retrograde beats."

It is seen from fig. 12, No 1, that with the numbers as given in the figure, it takes the time of 7 auricular systolæ after the extrasytole before the normal rhythm is restored again. For the special instant of the extrasystole of No. 2 and for the corresponding T_1, T_2, and P, the transient period

lasts about three auricular beats. Again, in Nos. 3 and 4, it takes respectively about 5·5 and 2·5 auricular periods before the normal action is restored again.

Finally, in fig. 13, two possible anomalies are depicted. Here, $T_1 > T_2$, *i. e.*, the natural ventricular free period is shorter than the auricular period. Thus the possibility arrives that the fundamental period of the complete system consists of a whole number of auricular systolæ, *i. e.*, the phenomenon repeats itself exactly only after, *e. g.*, 4 or 5 or 6 auricular beats. This fundamental period is indicated by the brackets underneath each drawing. We therefore find the possibility of a, *e. g.*, 2 : 3 block and a 5 : 7 block. We are not aware whether these phenomena occur in the real heart.

From the fact that, when

$$T_1 > T_2,$$

a forced ventricular beat can only occur when the stimulus from the A–V bundle arrives at the ventricle when the latter is outside its refractory period, it follows that the fundamental period T, where

$$T = nT_1,$$

is determined by the following two *Diophantic inequalities*

$$R < (nT_1 - mT_2) < T_2,$$

where both n and m are whole numbers and n the smallest possible one satisfying the inequalities.

Eindhoven, Natuurkundig Laboratorium
der N. V. Philips' Gloeilampen-fabrieken.
May 1928.

LXXIII. *On the Adsorption of the Alkali Metals on a Mercury-Vacuum Interface.* *By* R. Stevenson Bradley, *B.A.**.

THE adsorption of vapours on the surface of mercury has recently excited considerable interest; the corresponding case of adsorption of metals dissolved in mercury has not yet been studied.

The most interesting amalgams, and those for which most results are available, are those of the alkali metals. Both

* Communicated by Prof. R. Whytlaw-Gray.

Schmidt * and Oppenheimer † have published values for the surface tension of alkali metal amalgams at low concentrations. The publication by Bent ‡ and Hildebrand of the activities of the dissolved metals enables the Gibbs surface excess Γ to be calculated.

$$\Gamma = \frac{-d\sigma}{2{\cdot}303\,\mathrm{RT}} d\log a_2,$$

where σ is the surface tension, a_2 the activity of the dissolved metal.

Hildebrand's equations refer to pure alkali metal as the reference state ; when the latter is transferred to infinitely dilute amalgams they become

$$\log \frac{a_2}{\mathrm{N}_2}\,\mathrm{Cs} = \frac{15620}{\mathrm{T}}\,\mathrm{N}_2$$

$$\log \frac{a_2}{\mathrm{N}_2}\,\mathrm{K} = \frac{11630}{\mathrm{T}}\,\mathrm{N}_2$$

$$\log \frac{a_2}{\mathrm{N}_2}\,\mathrm{Na} = \left(\frac{3930}{\mathrm{T}} + 6{\cdot}84\right)\mathrm{N}_2,$$

where N_2 is the mol fraction of dissolved metal. This transference is equivalent to the omission of the constant C, which disappears on differentiating. There appears to be a misprint on p. 3024 of Hildebrand's paper; the coefficients of N_2 should be changed in sign in the three equations for $\log \frac{a_2}{\mathrm{N}_2}$.

The temperature has been taken as 18° C. Schmidt worked at about 18° C., Oppenheimer at 20 C. Temperature variations of a few degrees do not affect the values for a_2.

When σ is plotted against $\log a_2$ a straight line is obtained, and this constancy of Γ down to the lowest concentrations used and over a concentration range of over a hundredfold for sodium, and over tenfold for potassium and cæsium, suggests that a unimolecular surface layer is formed, even at 0·0007 per cent. of the alkali metals. At still lower concentrations the curve must bend sharply, and run nearly parallel to the axis of $\log a_2$.

In Tables I., II., and III., the fourth column gives the value of σ read off from the graph at the corresponding value of $\log a_2$.

* *Ann. der. Physik,* xxxix. p. 1108 (1912).
† *Zeitschr. f. Anorg. Chem.* clxxi. p. 98 (1928).
‡ J. Amer. Chem. Soc. xlix. p. 3011 (1927).

TABLE I.

Sodium Amalgams.

Wt. % Na.	σ.	$-\log a_2$.	corrected σ.
0·0002	435·5	4·76	435·2
0·0007	424·2	4·21	426·1
0·0022	418·8	3·71	417·7
*0·019	404·0	2·75	401·7
*0·025	399·0	2·62	399·4
0·049	393·3	2·28	393·7
0·067	391·3	2·12	391·0
0·124	384·4	1·77	385·3

GRAPH I.

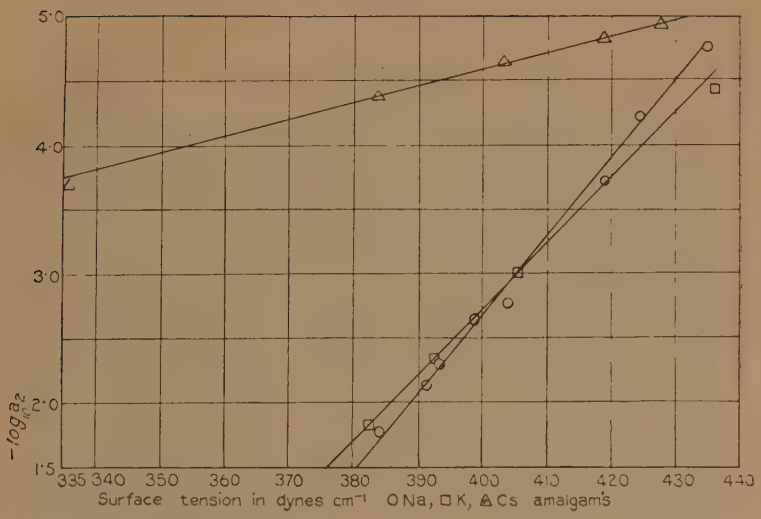


TABLE II.

Potassium Amalgams.

Wt. % K.	σ.	$-\log a_2$.	corrected σ.
0·0007	436·0	4·44	433·9
0·0018	405·1	3·00	405·4
0·0068	392·3	2·32	392·3
0·0135	388·4	1·88	383·6
0·015	382·5	1·81	382·3

* Values are those of Oppenheimer.

TABLE III.

Cæsium Amalgams.

Wt. °/₀ Cs.	σ.	$-\log a_2$.	corrected σ.
0·0008	427·6	4·92	426·2
0·001	418·8	4·82	418·5
0·0016	403·1	4·62	403·1
0·0028	383·5	4·37	383·6
0·0131	335·4	3·69	332·0

From the straight lines values of Γ may readily be calculated ; for sodium, potassium, and cæsium we find for $\frac{1}{\Gamma}$ in A.U. per atom the values,

55·4 47·9 14·7

These afford an interesting confirmation of the view that the deviations of the alkali metal amalgams from the perfect solution are to be attributed to compound formation. Bragg * gives for the atomic radii of sodium, potassium, and cæsium the values 1·77, 2·07, and 2·37 A.U. respectively, whilst Kolkmeyer † assigns 1·51 A.U. to mercury. We may assume that for sodium amalgams each atom of the surface is surrounded by six others. The area occupied by each atom may be taken as that of the circumscribing hexagon. This gives for the area occupied by the complex $Na-Hg_6$, in which each sodium atom is surrounded by a ring of six mercury atoms, the value 58 A.U. There are thus roughly six mercury atoms to one sodium atom on the surface. For potassium the ratio is less. This agrees with the freezing-point data of Kurnakow ‡, the stability of the compounds $R-Hg_4$, $R-Hg_2$, being greater, as measured by the degree of sharpness of the maxima, for sodium than for potassium. The value 14·8 A.U. for cæsium is less than that of the circumscribing hexagon 22·0 A.U. The constancy of Γ with varying concentrations makes the possibility of a poly-molecular layer unlikely, so that presumably the cæsium atoms are more tightly packed than in the crystal.

* Phil. Mag. xl. p. 169 (1920).
† *Rec. Trav. Pays Bas,* xliii. p. 677 (1924).
‡ *Zeitschr. f. Anorg. Chem.* xxiii. p. 439 (1900).

Summary.

For the amalgams of the metals sodium, potassium, and cæsium at low concentrations $\frac{d\sigma}{d(\log a_2)}$ is constant. Values of Γ, the surface excess, are in agreement with compound formation in the surface-layer, roughly to the extent of $Na-Hg_6$ for sodium, rather less for potassium. Cæsium atoms alone occupy the surface of cæsium amalgams.

The University,
Leeds.

LXXIV. *On the Application of Tensor Analysis to Physical Problems.* *By* Francis D. Murnaghan, *Professor of Applied Mathematics, Johns Hopkins University* *.

ALTHOUGH the methods of tensor analysis are generally admitted to be of great power and usefulness from a theoretical point of view, these methods are not commonly applied to problems in what may be called the older physics, the simple reason being that they are supposed to lead to expressions of too high a degree of complexity. We propose to treat in this paper the problem of determining the form of the stress-equations of elasticity in any system of curvilinear coordinates, orthogonal or not, and we trust that a comparison of our method with that given in Love's standard treatise † for the special case of orthogonal curvilinear coordinates will show that the methods of tensor analysis are not only more general but easier to follow than the method given there.

Before proceeding to a consideration of the particular problem with which we wish to support our thesis, it is necessary to point out that in physics we measure quantities that are usually different from the quantities met with in tensor analysis. Thus we say in the latter theory that if a set of n quantities X^r are the components of a contravariant tensor of the first rank in a coordinate system x, then the

* Communicated by the Author.

† A. E. H. Love, 'The Mathematical Theory of Elasticity,' 3rd edition, pp. 87–89.

components in any other coordinate system $\bar{x}$ are given by the equations

$$\bar{X}^r = X^\alpha \frac{\partial \bar{x}^r}{\partial x^\alpha} \quad (\alpha \text{ is a summation symbol}).$$

If we wish to give a geometrical interpretation to this description of a tensor, we may consider, from the x coordinate system, the family of level surfaces $\bar{x}^r = \text{const.}$; then the n expressions $\partial \bar{x}^r / \partial x^\alpha$ are, at any point x, the covariant components of the gradient vector to that particular level surface of the family which passes through the point in question. The magnitude of this gradient vector is

$$\left(g^{\alpha\beta} \frac{\partial \bar{x}^r}{\partial x^\alpha} \frac{\partial \bar{x}^r}{\partial x^\beta} \right)^{\frac{1}{2}},$$

where the g^{rs} are the contravariant components of the metrical tensor, and, in accordance with the formulæ of transformation for the components of a contravariant tensor, this is simply $(\bar{g}^{rr})^{\frac{1}{2}}$. Upon dividing our equation for $\bar{X}^r$ by this magnitude, we see that the ratio $\bar{X}^r/(\bar{g}^{rr})^{\frac{1}{2}}$ is the resolved part of the tensor X^r in the direction of the gradient vector to the $\bar{x}^r$ coordinate surface. Now, it is these resolved parts of tensors, *i. e.* these scalar quantities, with which we actually deal in physics. Since the gradient vector of any surface has the direction of the normal to the surface, drawn in the direction towards which the constant of the surface is increasing, the resolved part of the tensor X^s in this direction may be conveniently represented by the symbol $\bar{N}_r$, and we have the relation

$$\bar{X}^r = (\bar{g}^{rr})^{\frac{1}{2}} \bar{N}_r.$$

If, then, we wish to translate a theorem of tensor analysis which involves the components of a contravariant tensor of the first rank into a form suitable for the practical purposes of physics, we should replace each component X^r of the tensor by $(g^{rr})^{\frac{1}{2}} N_r$, where N_r denotes the resolved part of the tensor in the direction of the normal to the coordinate surface $x^r = \text{const.}$, the normal being drawn in the direction towards which x^r is increasing. Similarly, if we consider the formulæ of transformation for the components of a covariant tensor of rank one, namely,

$$\bar{X}_r = X_\alpha \frac{\partial x^\alpha}{\partial \bar{x}^r},$$

we see that the n quantities $\partial x^\alpha / \partial \bar{x}^r$, which appear as

coefficients in the rth of these formulæ, are the contravariant components of a tensor which is tangent to the $\bar{x}^r$ coordinate curve, *i. e.* the curve along which all the coordinates $\bar{x}$, save $\bar{x}^r$, are constant. The magnitude of this tensor is

$$\left(g_{\alpha\beta}\frac{\partial x^\alpha}{\partial \bar{x}^r}\frac{\partial x^\beta}{\partial \bar{x}^r}\right)^{\frac{1}{2}},$$

or simply $(\bar{g}_{rr})^{\frac{1}{2}}$, since the g_{rs} are the covariant components of the metrical tensor. Upon dividing our equation for $\bar{\mathrm{X}}_r$ by this magnitude, we see that the ratio $\bar{\mathrm{X}}_r/\bar{g}_{rr}^{\frac{1}{2}}$ is the resolved part of the covariant tensor X_r in the direction of the tangent to the $\bar{x}^r$ coordinate curve through the point in question, the tangent being supposed drawn in the direction in which $\bar{x}^r$ is increasing. This resolved part may be conveniently denoted by $\bar{\mathrm{T}}_r$, and we then have the equation

$$\bar{\mathrm{X}}_r = (\bar{g}_{rr})^{\frac{1}{2}}\bar{\mathrm{T}}_r.$$

If, then, we wish to translate a theorem of tensor analysis, which involves the components of a covariant tensor of rank one, into a form which is of practical utility for physics, we must replace each covariant component X_r by $(g_{rr})^{\frac{1}{2}}\mathrm{T}_r$, where T_r denotes the resolved part of the tensor in the direction of the tangent to the x^r coordinate curve through the point in question, the tangent being drawn in the sense in which x^r is increasing.

As examples of what we mean, let us consider two particular results :—

(a) In tensor analysis we have, associated with any contravariant tensor field X^r of rank one, a scalar quantity known as its divergence. The formal expression for this divergence is

$$\frac{1}{\sqrt{\bar{g}}}\frac{\partial}{\partial x^\alpha}(\sqrt{\bar{g}}\,\mathrm{X}^\alpha)^*.$$

We rewrite this expression in the form

$$\frac{1}{\sqrt{\bar{g}}}\frac{\partial}{\partial x^\alpha}(\sqrt{g}\overline{g^{\alpha\alpha}}\,\mathrm{N}_\alpha).$$

When the curvilinear coordinate system x is orthogonal, we may put

$$(ds)^2 = (dx')^2/h_1^2 + (dx^2)^2/h_2^2 + \ldots + (dx^n)^2/h_n^2,$$

* Here, as elsewhere throughout this paper, summation symbols are denoted by Greek letters.

so that

$$g_{rr} = (1/h_r)^2 \; ; \quad g_{rs} = 0 \; (r \neq s) \; ; \quad g = (1/h_1 h_2 \ldots h_n)^2$$

and

$$g^{rr} = h_r^2 \; ; \quad g^{rs} = 0 \; (r \neq s).$$

On substituting from these equations, we obtain the familiar formula for the divergence of a vector field in orthogonal curvilinear coordinates, namely

$$h_1 h_2 \ldots h_n \left\{ \frac{\partial}{\partial x^1}(\mathrm{N}_1/h_2 \ldots h_n) + \frac{\partial}{\partial x^2}(\mathrm{N}_2/h_1 h_3 \ldots h_n) + \ldots \right.$$
$$\left. + \frac{\partial}{\partial x^n}(\mathrm{N}_n/h_1 \ldots h_{n-1}) \right\}$$

(see Love, *loc. cit.* p. 54, eq. 37). It should be observed that when the coordinates are orthogonal the gradient vector to the coordinate surface x^r has the same direction as the coordinate line x^r, so that we could have written T_r instead of N_r in the expression for the divergence.

(*b*) Associated with any covariant vector field X_r we have an alternating covariant tensor field of rank two, which is known as the curl of the given tensor field. Its components X_{rs} are defined by the equations

$$\mathrm{X}_{rs} = \partial \mathrm{X}_s/\partial x^r - \partial \mathrm{X}_r/\partial x^s.$$

In accordance with our remarks above, the X_r which occur on the right-hand side of these formulæ must be replaced by $(g_{rr})^{\frac{1}{2}}\mathrm{T}_r$, but it is necessary to find out what physically measured quantities are described by the components X_{rs} of the alternating covariant tensor of rank two. From the formulæ of transformation we have

$$\bar{\mathrm{X}}_{rs} = \mathrm{X}_{\alpha\beta}\frac{\partial x^\alpha}{\partial \bar{x}^r}\frac{\partial x^\beta}{\partial \bar{x}^s} = {}'\mathrm{X}_{\alpha\beta}\frac{\partial(x^\alpha, x^\beta)}{\partial(\bar{x}^r, \bar{x}^s)},$$

where the prime indicates that the summation labels α and β run over all pairs, without repetition, out of the n labels 1 to n. The $n(n-1)/2$ Jacobian determinants may be said to define an element of area on the $(\bar{x}^r, \bar{x}^s)$ coordinate surface, *i. e.* the surface on which all the coordinates $\bar{x}$, save $\bar{x}^r$ and $\bar{x}^s$, are constant. The magnitude of this element of area is, by definition, the square root of

$${}'(g_{\alpha\lambda}g_{\beta\mu} - g_{\alpha\mu}g_{\beta\lambda})\frac{\partial(x^\alpha, x^\beta)}{\partial(\bar{x}^r, \bar{x}^s)}\frac{\partial(x^\lambda, x^\mu)}{\partial(\bar{x}^r, \bar{x}^s)},$$

where the summation labels (α, β) and (λ, μ) run, independently, without repetition over all pairs out of the n labels 1 to n. If we introduce the symbol

$$g_{pq,\,rs} = \begin{vmatrix} g_{pr} & g_{ps} \\ g_{qr} & g_{qs} \end{vmatrix} = g_{pr}g_{qs} - g_{ps}g_{qr},$$

this is a covariant tensor of rank four, which is alternating in the first two labels (pq) and also in the last two (rs). Our expression for the magnitude of the element of area takes the form

$$\left\{ {}' g_{\alpha\beta,\,\lambda\mu} \frac{\partial(x^\alpha, x^\beta)}{\partial(\bar{x}^r, \bar{x}^s)} \frac{\partial(x^\lambda, x^\mu)}{\partial(\bar{x}^r, \bar{x}^s)} \right\}^{\frac{1}{2}},$$

or simply $(\bar{g}_{rs,\,rs})^{\frac{1}{2}}$, from the formulæ of transformation for a covariant tensor of rank four. If, then, we divide our equation for $\bar{\mathrm{X}}_{rs}$ by this magnitude, the result is the flux of the alternating tensor X_{rs} through the element of area of the $(\bar{x}^r, \bar{x}^s)$ coordinate surface divided by the magnitude of this element of area. We shall denote this by $\bar{\mathrm{T}}_{rs}$, and may call it the resolved part of the tensor X_{rs} in the direction of the $(\bar{x}^r, \bar{x}^s)$ coordinate surface. We have the equation of connexion

$$\bar{\mathrm{X}}_{rs} = (\bar{g}_{rs,\,rs})^{\frac{1}{2}} \bar{\mathrm{T}}_{rs},$$

or, in the x coordinate system,

$$\mathrm{X}_{rs} = (g_{rs,\,rs})^{\frac{1}{2}} \mathrm{T}_{rs} = (g_{rr}g_{ss} - g_{rs}^2)^{\frac{1}{2}} \mathrm{T}_{rs}.$$

Hence the desired, physically useful, form of the equations of definition of the curl of a covariant tensor field of rank one is

$$\mathrm{T}_{rs} = (g_{rr}g_{ss} - g_{rs}^2)^{-\frac{1}{2}} \left\{ \frac{\partial}{\partial x^r}(g_{ss}^{\frac{1}{2}} \mathrm{T}_s) - \frac{\partial}{\partial x^s}(g_{rr}^{\frac{1}{2}} \mathrm{T}_r) \right\}.$$

In the special case of orthogonal curvilinear coordinates this takes the form

$$\mathrm{T}_{rs} = h_r h_s \left\{ \frac{\partial}{\partial x^r}(\mathrm{T}_s/h_s) - \frac{\partial}{\partial x^s}(\mathrm{T}_r/h_r) \right\}$$

(*cf.* Love, *loc. cit.* p. 55, formulæ 38).

We now proceed to a consideration of the stress-equations of elasticity theory. The rôle of the stress-tensor is that of associating with any element of area at a point a vector which is the stress, or force, per unit area, across that element. In the usual presentation of the theory the stress-tensor is given as a tensor of the second rank, and when

rectangular Cartesian coordinates are used the nine components are denoted by the scheme

$$\begin{pmatrix} X_x & X_y & X_z \\ Y_x & Y_y & Y_z \\ Z_x & Z_y & Z_z \end{pmatrix}.$$

Thus X_y, for example, denotes the x-component of the stress across an element which is placed perpendicular to the v-axis. It is assumed that the stress-tensor is symmetric, so that we have the three relations

$$Y_z = Z_y; \quad Z_x = X_z; \quad X_y = Y_x.$$

The stress-equations are

$$\partial X_x/\partial x + \partial X_y/\partial y + \partial X_z/\partial z = \rho(\ddot{x} - X),$$
$$\partial Y_x/\partial x + \partial Y_y/\partial y + \partial Y_z/\partial z = \rho(\ddot{y} - Y),$$
$$\partial Z_x/\partial x + \partial Z_y/\partial y + \partial Z_z/\partial z = \rho(\ddot{z} - Z)$$

(*cf.* Love, *loc. cit.* p. 33), and it is our purpose to rewrite these equations when the coordinates in use are any set of curvilinear coordinates whatever.

Since the rôle of the stress-tensor is to set up a correspondence between elements of area and vectors, the stress-tensor must be covariant of rank two and contravariant of rank one; in all, it is of rank three, and it is alternating in the two covariant labels. Denoting it by $X_{pq}{}^r$, we have

$$X_{qp}{}^r = -X_{pq}{}^r.$$

The vector, or contravariant tensor of rank one, associated by means of the stress-tensor with any element of area is

$$X^r = {}'X_{\alpha\beta}{}^r \, d(x^\alpha, x^\beta),$$

where the $n(n-1)/2$ Jacobian determinants $d(x^\alpha, x^\beta)$ serve to define the element of area. In order, however, to conform with the usual practice of representing the stress-tensor as a tensor of rank two, we multiply the triply-labelled tensor $X_{pq}{}^r$ scalarly by the alternating tensor ϵ^{lmn}, whose components have the values $\pm 1/g^{\frac{1}{2}}$ or zero, and arrive in this way at the contravariant tensor of rank two,

$$X^{sr} = \tfrac{1}{2}\epsilon^{s\alpha\beta} X_{\alpha\beta}{}^r = (X_{pq}{}^r)/\sqrt{g}.$$

Here p and q are the two labels which are different from s,

arranged so that the arrangement $(s\,p\,q)$ is an even rearrangement of the standard order (123). Explicitly

$$X^{1r} = (X_{23}{}^{r}) / \sqrt{g}\,; \quad X^{2r} = (X_{31}{}^{r}) / \sqrt{g}\,; \quad X^{3r} = (X_{12}{}^{r}) / \sqrt{g}.$$

This doubly-labelled tensor X^{sr} may be called the contravariant stress-tensor of rank two. It is then apparent that the stress-equations already given are merely the rectangular Cartesian form of the tensor-equation

$$X^{sa}{}_{,\,a} + F^{s} = 0,$$

where the symbol $X^{sa}{}_{,\,a}$ means that we first take the covariant derivative $X^{sr}{}_{,\,t}$ of X^{sr} and then contract with respect to the labels r and t. The tensor F^{s} is the contravariant presentation of the tensor whose components in rectangular Cartesian coordinates are

$$\rho(X - \ddot{x}), \quad \rho(Y - \ddot{y}), \quad \rho(Z - \ddot{z}).$$

We shall call this the force tensor per unit volume, in accordance with D'Alembert's scheme of reducing a dynamical problem to a static one by including amongst the forces acting on the system the reversed inertial forces. As far as tensor analysis goes, the problem is over; the stress-equations in any coordinate system whatever are

$$X^{sa}{}_{,\,a} + F^{s} = 0.$$

In order, however, to put this result in a form which may be useful in practice, we must ask ourselves how the components X^{sr} of the contravariant stress-tensor are connected with the stresses which are actually measured. In order to answer this question, we shall first consider the stress-tensor in the form in which it actually arises, *i. e.* in its triply-labelled form $X_{pq}{}^{r}$. When a transformation to any other coordinate system $\bar{x}$ is made, the components of the stress-tensor become

$$\bar{X}_{pq}{}^{r} = {}'X_{\alpha\beta}{}^{\delta} \frac{\partial(x^{\alpha}, \bar{x}^{\beta})}{\partial(\bar{x}^{p}, \bar{x}^{q})} \frac{\partial \bar{x}^{r}}{\partial x^{\delta}},$$

where the prime indicates that the summation labels (α, β) run over the three pairs (2, 3), (3, 1), and (1, 2) without repetition. If we divide this equation through by the magnitude

$$\left\{ {}'g_{\alpha\beta,\,\lambda\mu} \frac{\partial(x^{\alpha}, x^{\beta})}{\partial(\bar{x}^{p}, \bar{x}^{q})} \frac{\partial(x^{\lambda}, x^{\mu})}{\partial(\bar{x}^{p}, \bar{x}^{q})} \right\}^{\frac{1}{2}}$$

of the element of area of the $(\bar{x}^p, \bar{x}^q)$ coordinate surface and also by the magnitude

$$\left\{ g^{\delta\epsilon} \frac{\partial \bar{x}^r}{\partial x^\delta} \frac{\partial \bar{x}^r}{\partial x^\epsilon} \right\}^{\frac{1}{2}}$$

of the contravariant tensor $\partial \bar{x}^r / \partial x^\delta$, which is tangent to the $\bar{x}^r$ coordinate line, we obtain the resolved part of the stress, *i. e.* force per unit area, across the element of area of the $(\bar{x}^p, \bar{x}^q)$ coordinate surface, in the direction of the $\bar{x}^r$ coordinate line. This resolved part of the stress may be denoted by the symbol $\widehat{\overline{pq}, r}$, and our equation for $\mathrm{X}_{pq}{}^r$ is equivalent to

$$\bar{\mathrm{X}}_{pq}{}^r = \sqrt{(\bar{g}_{pp}\bar{g}_{qq} - \bar{g}_{pq}{}^2)\bar{g}^{rr}}\ \widehat{\overline{pq}, r}.$$

Upon multiplying this through by $1/\bar{g}^{\frac{1}{2}}$, we find

$$\bar{\mathrm{X}}^{sr} = \sqrt{(\bar{g}_{pp}\bar{g}_{qq} - \bar{g}_{pq}{}^2)\bar{g}^{rr}/\bar{g}}\ \widehat{\bar{s}\bar{r}},$$

where (s, p, q) is an even rearrangement of $(1, 2, 3)$ and $\widehat{\bar{s}\bar{r}}$ denotes precisely the same physically measured thing as $\widehat{\overline{pq}, r}$. Dropping now the bars, we see that

$$\mathrm{X}^{sr} = \sqrt{(g_{pp}g_{qq} - g_{pq}{}^2)g^{rr}/g}\ \widehat{sr} = \sqrt{g^{ss}g^{rr}}\ \widehat{sr},$$

since

$$g^{ss} = (g_{pp}g_{qq} - g_{pq}{}^2)/g.$$

These are the expressions that must be substituted for X^{sr} in the equations $\mathrm{X}^{sa}{}_{,a} + \mathrm{F}^s = 0$ to make them practically useful. Even when this is done, there is one further step to take. Since the F^s are the components of a contravariant tensor of rank one, we write them in the form

$$\mathrm{F}^s = (g^{ss})^{\frac{1}{2}}\mathrm{N}_s,$$

and obtain the desired form of the stress-equations:

$$\left.\begin{aligned} &(g^{ss})^{-\frac{1}{2}}\mathrm{X}^{sa}{}_{,a} + \mathrm{N}_s = 0, \\ &\mathrm{X}^{sr} = \sqrt{(g_{pp}g_{qq} - g_{pq}{}^2)g^{rr}/g}\ \widehat{sr} \\ &\qquad = \sqrt{g^{ss}g^{rr}}\ \widehat{sr}. \end{aligned}\right\}$$

Here (s, p, q) is an even rearrangement of $(1, 2, 3)$, and N_s denotes the resolved part of the force-tensor along the normal to the coordinate surface $x^s = \text{const.}$ We may put this result in a somewhat more explicit form. Thus, from the formula for covariant differentiation, we have

$$\mathrm{X}^{sr}{}_{,t} = \partial \mathrm{X}^{sr}/\partial x^t + \mathrm{X}^{\beta r}\Gamma_{\beta t}{}^s + \mathrm{X}^{s\beta}\Gamma_{\beta t}{}^r,$$

where the $\Gamma_{pq}^{\ r}$ are the Riemann-Christoffel three index symbols of the second kind. Hence

$$\begin{aligned} X^{s\alpha}{}_{,\,\alpha} &= \partial X^{s\alpha}/\partial x^{\alpha} + X^{\beta\alpha}\,\Gamma_{\beta\alpha}^{\ \ s} + X^{s\beta}\,\Gamma_{\beta\alpha}^{\ \ \alpha} \\ &= \partial X^{s\alpha}/\partial x^{\alpha} + X^{\beta\alpha}\,\Gamma_{\beta\alpha}^{\ \ s} + X^{s\beta}\frac{\partial}{\partial x^{\beta}}\log\sqrt{g} \\ &= \frac{1}{\sqrt{g}}\frac{\partial}{\partial x^{\alpha}}(\sqrt{g}\,X^{s\alpha}) + X^{\beta\alpha}\,\Gamma_{\beta\alpha}^{\ \ s}. \end{aligned}$$

In the particular case of orthogonal curvilinear coordinates, where

$$(ds)^2 = (dx^1)^2/h_1^{\,2} + \ldots + (dx^n)^2/h_n^{\,2},$$

$$\Gamma_{11,1} = \tfrac{1}{2}\partial g_{11}/\partial x^1 = -(\partial h_1/\partial x^1)/h_1^{\,3};$$

$$\Gamma_{11}^{\ 1} = g^{11}\,\Gamma_{11,1} = -(\partial h_1/\partial x^1)/h_1;$$

$$\Gamma_{11,2} = -\tfrac{1}{2}\partial g_{11}/\partial x^2 = (\partial h_1/\partial x^2)/h_1^{\,3};$$

$$\Gamma_{11}^{\ 2} = g^{22}\,\Gamma_{11,2} = (h_2^{\,2}\,\partial h_1/\partial x^2)/h_1^{\,3};$$

$$\Gamma_{12,1} = \Gamma_{21,1} = \tfrac{1}{2}\partial g_{11}/\partial x^2 = -(\partial h_1/\partial x^2)/h_1^{\,3};$$

$$\Gamma_{12}^{\ 1} = \Gamma_{21}^{\ 1} = g^{11}\,\Gamma_{12,1} = -(\partial h_1/\partial x^2)/h_1;$$

$$\Gamma_{12,3} = 0; \qquad \Gamma_{12}^{\ 3} = g^{33}\,\Gamma_{12,3} = 0,$$

$$X^{11} = h_1^{\,2}\,\widehat{11}; \qquad X^{12} = h_1 h_2\,\widehat{12}; \qquad X^{13} = h_1 h_3\,\widehat{13}, \quad \text{etc.}$$

Since the contravariant stress-tensor is symmetric, these equations show that $\widehat{sr} = \widehat{rs}$. On putting $s=1$, the first of our three equations becomes

$$\begin{aligned} N_1 + \frac{1}{h_1}\Big\{ & h_1 h_2 h_3\Big[\frac{\partial}{\partial x^1}(h_1\,\widehat{11}/h_2 h_3) + \frac{\partial}{\partial x^2}(\widehat{12}/h_3) + \frac{\partial}{\partial x^3}(\widehat{13}/h_2)\Big] \\ & - h_1\,\widehat{11}\,\partial h_1/\partial x^1 - 2h_2\,\widehat{12}\,\partial h_1/\partial x^2 - 2h_3\,\widehat{13}\,\partial h_1/\partial x^3 \\ & + h_1^{\,2}\,\widehat{22}\,(\partial h_2/\partial x^1)/h_2 + h_1^{\,2}\,\widehat{33}\,(\partial h_3/\partial x^1)/h_3\Big\} = 0, \end{aligned}$$

i. e.

$$\begin{aligned} N_1 + h_1 h_2 h_3 \Big\{ & \frac{\partial}{\partial x^1}(\widehat{11}/h_2 h_3) + \frac{\partial}{\partial x^2}(\widehat{12}/h_3 h_1) + \frac{\partial}{\partial x^3}(\widehat{13}/h_1 h_2)\Big\} \\ & + \widehat{12}\,h_1 h_2\frac{\partial}{\partial x^2}(1/h_1) + \widehat{13}\,h_1 h_3\frac{\partial}{\partial x^3}(1/h_1) \\ & - \widehat{22}\,h_1 h_2\frac{\partial}{\partial x^1}(1/h_2) - \widehat{33}\,h_1 h_3\frac{\partial}{\partial x^1}(1/h_3) = 0 \end{aligned}$$

(*cf.* Love, *loc. cit.* p. 89, formula 19).

It would be somewhat pedantic to point out that the argument as outlined here is applicable to tensors of any rank provided they are *alternating*. Indeed, it may not be too much to say that alternating tensors suffice for physics; the underlying reason therefore being that the elements of content, *i. e.* area, volume, etc., are described by means of Jacobian determinants, which are in their very nature alternating. The obvious rejoinder to such a remark is a reference to the contravariant stress-tensor X^{sr}, which is, as we have remarked above, symmetric. However, the stress-tensor should really be regarded in its triply-labelled form $X_{pq}{}^{r}$, the doubly-labelled form X^{sr} being artificial. To say that $X^{32}=X^{23}$, for instance, is to say that $X_{12}{}^{3}=X_{31}{}^{3}$, or, equivalently, that $X_{12}{}^{2}+X_{13}{}^{3}=0$, since the stress-tensor is alternating in its covariant labels. Expressed in tensor form, this says that the result of contracting the triply-labelled stress-tensor is the zero-tensor, *i. e.*

$$X_{pa}{}^{a} = 0.$$

A similar remark would apply to the symmetrical tensor G_{rs}, which, in Einstein's theory, vanishes in space at points free from matter. This may be presented as a tensor of rank four, $G_{lmn}{}^{r}$, which is alternating in the covariant labels. The condition of symmetry is

$$G_{lma}{}^{a} = 0.$$

LXXV. *A General Theorem on Screened Impedances.* *By* Raymond M. Wilmotte, *B.A.* (*of the National Physical Laboratory*)*.

Summary.

For accurate measurements, especially at high frequencies, it is necessary that all impedances and apparatus used should be surrounded by metal screens kept at definite potentials. By this means, the leakage and capacity effects to earth can be rendered perfectly definite, and the apparatus electrically independent of the surrounding objects. Even when this is done, there is some ambiguity regarding the value of the impedance of the apparatus. The impedance is

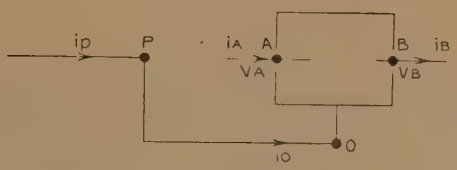
* Communicated by the Author.

the ratio of the potential difference across the apparatus to the current. Now, both the potential difference and the current depend on the potential of the screen; moreover, the current may be measured at various points. One of the most usual values of the impedance is obtained when the screen is kept at the same potential as the terminal where the current is being measured, but is not directly connected to that terminal. On this definition of impedance it would be natural to expect that there would be two possible values, depending on which terminal is kept at the potential of the screen. In this paper the curious result is obtained that these two values are equal, and certain limitations are considered. This general result is of considerable importance, as it makes it unnecessary to connect the apparatus in any special way, so long as the screen is kept at the same potential as the terminal at which the current is measured.

Introduction.

CAPACITY effects to earth have brought about the universal use of metal screens surrounding any apparatus which is to be used for accurate measurements, especially at

Fig. 1.



high frequencies. The only case in which it is legitimate to do without metal screens is when the impedance of the apparatus is small.

Generally, then, an impedance has three terminals—one at each end, and one on the screen. Let these be A, B, and O respectively, as shown in fig. 1.

The value of the impedance is the ratio of the potential difference between A and B to the current. This will depend on the potential at which the shield O is kept relatively to A or B, and the point at which the current is measured. The screen S is usually connected to some point P in the circuit. This point P is not necessarily directly connected to A or B, but is instrumental in fixing the potential of O relative to A or B. For any setting

of the potential of the screen O relative to A, there will be two possible values of the impedance, namely,

$$\frac{V_A - V_B}{i_A} \quad \text{and} \quad \frac{V_A - V_B}{i_B}.$$

If the screen O is given the same setting of potential but relative to B instead of to A, there should be another two values for the impedance:

$$\frac{V_A' - V_B'}{i_A'} \quad \text{and} \quad \frac{V_A' - V_B'}{i_B}$$

It is proved in the next paragraph that the only setting of the potential of O which will make two of these values equal in the general case is when the potential of O is made equal to that of A or B, then

$$\frac{V_A - V_B}{i_A} = \frac{V_A' - V_B'}{i_B'} \quad \ldots\ldots \quad (1)$$

For any special case, of course, some of the values of the impedance can be made equal by suitable settings of the potential of the screen; for instance, if there is absolute symmetry about the centre of the impedance, it will also be found that

$$\frac{V_A - V_B}{i_B} = \frac{V_A' - V_B'}{i_A'}.$$

In this particular case, then, the values of the impedance can be be reduced to two.

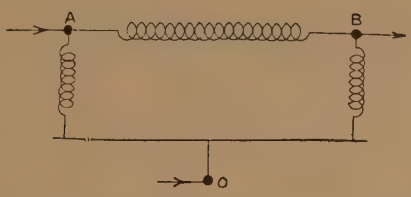
The importance of the equality (1) in the general case is that the impedance of any piece of apparatus can be given without stating which terminal should be kept at the potential of the screen. The potential of the screen must be kept at the potential of one of the terminals A or B, and the screen must not be directly connected to that terminal. This latter condition is necessary, for if the point P coincides with A, the current measured would not be I_A, but I_P.

The condition, that the screen should be kept at the potential of one of the terminals while there is no direct connexion between the two, happens to be a very frequent condition of bridge measurements where a Wagner earth is used. It would be convenient, therefore, to standardize this particular value of the impedance so that only when other values are required should it be necessary to state the conditions of measurement.

Two other values, sometimes required, occur when the screen is directly connected to one of the terminals. That is, P coincides with either A or B. If P coincides with A, the current I_B should be measured and not I_P. The reason for this is that, owing to the comparatively large size of the screen, appreciable current may flow *vid* the earth to the screen from other apparatus in the circuit, and the current I_P will depend not only on the potential difference between A and B, but also on the circuit arrangement. On the other hand, the current i_B is independent of the circuit, being equal to $(i_A + i_0)$.

The three common values of an impedance can be represented diagrammatically by a network of three impedances, as shown in fig. 2. This method of representation may be useful in some cases (*e. g.*, a condenser) in order to gain a physical conception why the different values exist; but, in general,

Fig. 2.



this is unnecessary, since in any case the complete data of the impedance of a piece of apparatus used in such a way that the screen is kept by some means or other at the potential of one of the terminals, must consist of at least three values.

The above results have been stated for a special case in a previous paper by L. Hartshorn and the author *, but no proof was given and the result was not generalized, nor were the limitations considered.

Proof.

Consider the impedance made of a network of admittances interconnecting the points 1, 2, 3, ... n, such that Y_{rs} is the admittance joining the points r and s. The points 1 and n correspond to the terminals of the apparatus. Let a current I_1 enter at the point 1 and I_n leave at the point n. Let V_1,

* L. Hartshorn & R. M. Wilmotte, "Note on Shielded Non-inductive Resistances," J. Sci. Inst. iv. pp. 33–37 (1926).

$V_2, V_3, \ldots, V_n$ be the potentials of the junction points of the admittances. Let the screen be denoted by the point O.

Since the the total current entering a junction point is zero, we have

$$I_1 = (V_0 - V_1)Y_{01} + (V_2 - V_1)Y_{12} + (V_3 - V_1)Y_{13} + \ldots + (V_n - V_1)Y_{1n}$$

$$= -V_1 \sum_{r=0}^{r=n} (Y_{1r}) + V_2 Y_{12} + V_3 Y_{13} + \ldots + V_n Y_{1n} + V_0 Y_{01}.$$

Similarly,

$$O = V_1 Y_{12} - V_2 \sum_{0}^{n} (Y_{2r}) + V_3 Y_{23} + \ldots + V_n Y_{2n} + V_0 Y_{02}$$

. . . . . .

$$-I_n = V_1 Y_{1n} + V_2 Y_{2n} + V_3 Y_{3n} + \ldots - V_n \sum_{0}^{n} (Y_{rn}) + V_0 Y_{0n}.$$

Eliminating $V_2, V_3, \ldots, V_{n-1}$ from the first $(n-1)$ equations, we obtain

$$I_1 \nabla = V_1 \nabla_1 + V_n \nabla_n + V_0 \nabla_0, \quad . \quad . \quad . \quad (2)$$

where

$$\nabla = \begin{vmatrix} -\sum_{0}(Y_{2r}), & Y_{23}, & \ldots\ldots, & Y_{2.n-1} \\ Y_{23}, & -\sum_{0}^{n}(Y_{3r}), & \ldots\ldots, & Y_{3.n-1} \\ \ldots & \ldots & \ldots & \ldots \\ Y_{2.n-1}, & Y_{3.n-1}, & \ldots\ldots, & -\sum_{0}^{n}(Y_{r.n-1}) \end{vmatrix}$$

and

$$\nabla_r = \begin{vmatrix} Y_{1r}, & Y_{12}, & Y_{13}, & \ldots\ldots, & Y_{1.n-1} \\ Y_{2r}, & -\sum_{0}^{n}(Y_{2r}), & Y_{23}, & \ldots\ldots, & Y_{2.n-1} \\ Y_{3r}, & Y_{23}, & -\sum_{0}^{n}(Y_{3r}), & \ldots\ldots, & Y_{3.n-1} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ Y_{n-1.r}, & Y_{2.n-1}, & Y_{3.n-1}, & \ldots\ldots, & -\sum_{0}^{n}(Y_{r.n-1}) \end{vmatrix}$$

It should be noted that both ∇ and ∇_n are symmetrical with respect to 1 and n, that is, 1 and n can be interchanged without changing their value. This symmetry does not

exist in ∇_0 or ∇_1. The following relation can also be shown to obtain

$$\nabla_0+\nabla_1+\nabla_n=0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now let V_0, the potential of the screen, be given a certain value between V_1 and V_n, so that it can be written in the form

$$V_0=V_1+k(V_n-V_1), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where k is a constant.

Equations (2), (3), and (4) reduce to

$$\frac{I_1}{V_n-V_1}=\frac{\nabla_n-k\,.\,\nabla_0}{\nabla}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The left-hand side of this equation is the admittance of the apparatus with the screen at a potential $k(V_n-V_1)$ above that of the point 1, and the current measured at the point 1. This value of the admittance will only be equal to the value when the screen is at a potential $k(V_n-V_1)$ above the point n and the current measured at n, if the right-hand side of equation (5) is symmetrical with respect to 1 and n. This will only occur for either of the two conditions:

(a) that ∇_0 be symmetrical with respect to 1 and n, or

(b) that $k=0$, that is, $V_0=V_1$.

The first of these conditions will only occur in special cases, while the second only means that the potential of the screen must be kept at the potential of one of the terminals. The admittance in this latter case is

$$\frac{\nabla_n}{\nabla}.$$

The effect on the admittance of measuring the current at the other terminal is equivalent to putting $k=1$ in equation (5). The admittance is then

$$\frac{\nabla_n-\nabla_0}{\nabla}.$$

This is not symmetrical with respect to 1 and n in the general case unless ∇_0 is symmetrical. There will, therefore, generally be two values for this admittance, depending on which terminal is kept at the potential of the screen.

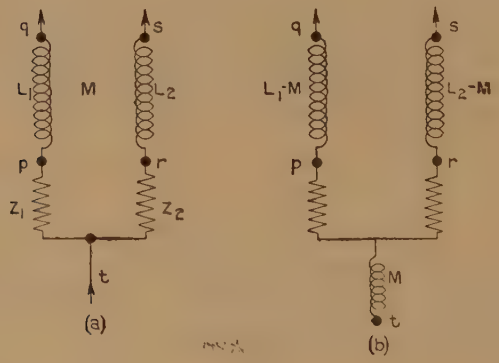
It may be noted that in the proof no restriction whatever was imposed on the nature or magnitude of the admittances, so that the result will hold even if the admittances to the

screen are not capacitative. Nor were there any limitations to the number of admittances. The existence of distributed admittances, therefore, will not invalidate the result.

Limitations.

In the proof given in the last paragraph, it has been tacitly assumed that the values of the admittances are the same whether $V_0 = V_1$ or V_n, although, admittedly, the current distribution will have altered. In other words, the potential difference between any two consecutive junction points must be proportional to the current flowing directly between those two points. It would appear, therefore, that mutual inductances within the apparatus would

Fig. 3.



invalidate the theorem. That this is so in a general case can be proved by working out a simple network. There, is, however, a condition in which the presence of mutual inductances does not affect the result, and these cases are so general that they will almost invariably be found in practice.

A mutual inductance, as in fig. 3 (*a*), between two coils *pq* and *rs*, which are joined at the point *t* through impedances Z_1 and Z_2, can be exactly represented by the network of impedances shown in fig. 3 (*b*), so long as the current in Z_1 is the same as that in L_1 and the current in Z_2 is the same as that in L_2. Such a mutual inductance, if present in an apparatus, can be replaced by its equivalent network, so that the theorem will still hold, as the assumption on which it depends is accurately correct.

In practice it often happens that the currents in Z_1 and L_1, or Z_2 and L_2, are not absolutely equal owing to small stray capacity effects. These will cause a deviation to the first order of small quantities. If, moreover, the mutual inductance is also small, the error will depend on the product of the capacity and the mutual inductance, and will only be of the second order.

Another effect that may invalidate the theorem is the presence of eddy currents. This is purely due to a mutual inductance between a coil and a lump of metal, and can be treated as an ordinary mutual inductance. The theorem will still be correct, therefore, if the coil is connected to the lump of metal through an impedance carrying the same current as the coil.

The final cause, owing to which the theorem will fail, is closely connected with the exact definition of potential difference. The lines of electric intensity are not solely due to the distribution of charges or current alone, but to a combination of the two. Any alteration of one which is not followed by a similar alteration in the other will affect the lines of flow of the displacement current in the dielectric, and will cause an alteration in the distribution of the capacities. In a general case, the distribution of capacities will differ with the potential of the screen. In all practical cases, however, this effect will be quite negligible, with certain exceptions, when the size of the apparatus is comparable to the wavelength.

10th July, 1928.

LXXVI. *On the Penetration of an Electric Field through Wire-gauze.* *By* W. B. Morton, *M.A.*, *Queen's University, Belfast* *.

IN a method which has been frequently used for the investigation of the mobilities of gaseous ions, the apparatus consists of a cylindrical vessel which is divided into two compartments by a partition of wire-gauze. Ions are generated in one compartment and are acted upon by a steady electric field which pushes them through the meshes of the gauze into the other compartment. Here they come under the influence of an alternating field. If this is strong

* Communicated by the Author.

enough, and the alternations slow enough, ions leaving the gauze will be carried to the plate which forms the other boundary of the field before they are turned back by the reversal of the electric force. The plate is connected to an electrometer; so that the current reaching it can be measured for different values of the alternating P.D. The mobility can be deduced from the value of the smallest field which can produce a current between gauze and plate.

The values arrived at by different workers vary rather widely and several suggestions have been made to account for this. Among these there is one on which special emphasis has been laid by Loeb *, namely, that a source of error is to be found in the interpenetration of the two fields through the meshes of the gauze. It is the object of the present note to examine this as a purely mathematical problem, with a view to finding an upper limit to the importance of this source of error. Any disturbance of the applied field due to the presence of the ions will be neglected and the ions will be supposed to move along the lines of force with a velocity proportional to the strength of the field at each point.

It seems obvious that the effect of the penetration of fields will be increased by each of the following three modifications of the actual experimental arrangement. These at the same time reduce the problem to a form easily tractable:

(1) Remove one set of wires of the gauze, so transforming it to a grating.
(2) Reduce the wires to mathematical lines.
(3) Consider only ions which move along lines of force midway between the wires.

In this way we shall arrive at a disturbance of the theoretical result greater than that to be expected under the actual conditions. It will appear that, even after this exaggeration, the error is only a small one. We require, to begin with, the field of a freely charged grating of thin parallel wires. This is contained in Maxwell's solution of the problem of electric screening by a grating. It may also be obtained as the limit of the case of plane strips regularly spaced in their own plane. It is easy to verify that the relation

$$\sin(x+iy) = \sin\delta\cosh(\phi+i\psi),$$

where ϕ is the potential, gives the field of a series of strips in the plane $y=0$ with spacing π, the breadth of a strip

* Loeb, Journ. Franklin Inst. v. 196, p. 771 (1923).

being 2δ. The force at a great distance from the grating is unity. The straight line of force $\psi=0$, $x=\frac{\pi}{2}$ passes through the centre of a space, the magnitude of the force along it is $\sinh y/(\cosh^2 y-\sin^2\delta)^{\frac{1}{2}}$, the line $\psi=\frac{\pi}{2}$, $x=0$ passes through the middle of a strip, magnitude of force is $\cosh y/(\sinh^2 y+\sin^2\delta)^{\frac{1}{2}}$. Making $\delta=0$, we find that the force due to a freely charged grating of thin wires, in a plane midway between wires, varies as $\tanh y$, when the distance between wires is π, or as $\tanh(\pi y/s)$ when the spacing is s. By superposing a uniform field perpendicular to the plane of the grating, we obtain a field which has values E_1, E_2 at great distances on the negative and positive sides respectively. The expression for the force along the midway line is then

$$\tfrac{1}{2}(E_2+E_1)+\tfrac{1}{2}(E_2-E_1)\tanh(\pi y/s).$$

We take E_1, on the negative side, to be the steady auxiliary field which pushes the ions through the gauze, and E_2, on the positive side, the alternating force by which the mobility is measured. The equation of motion of an ion is got by equating dy/dt to k times the above expression, where k is the mobility.

Two methods have been adopted in practice as regards the alternating field: (1) the "square-wave" plan, in which, by means of a commutator, the force E_2 is suddenly changed from a constant value in one direction to a constant value in the opposite direction; (2) the sine-wave method, in which E_2 is given by an alternator. In the first case the equation of motion can be integrated; in the second case the variables cannot be separated, and recourse must be had to either arithmetical or geometrical methods. I have used the latter to obtain approximations which are, perhaps, close enough for the present purpose.

(1) When E_2 is constant the integral is

$$2\pi k E_1 E_2 t$$
$$= s\{(E_2+E_1)\eta-(E_2-E_1)\log(E_2e^{\eta}+E_1e^{-\eta})\}+\text{const.}$$

in which η is written for $\pi y/s$.

Suppose the force to continue at the constant value E_2 for time T in the direction which moves the ion away from the gauze. Then the distance, if the gauze introduced no

disturbance of the field, would be $kF_2T=c$, say. Put $\pi c/s=\gamma$. We want to compare with c the actual distance reached in time T by an ion which starts from the plane of the gauze, or to compare η with γ. Writing p for the ratio E_2/E_1, we arrive at the result :

$$(p+1)\eta-(p-1)\{\log(pe^{\eta}+e^{-\eta})-\log(p+1)\} = 2\gamma.$$

The disturbance vanishes when $E_1=E_2$, or $p=1$. It will be seen that the above equation then gives $\eta=\gamma$.

The equation becomes simpler when $e^{-\eta}$ can be neglected, and this is allowable in the conditions of experiment. $e^{-\eta}$ is less than ·01 when $\eta>4{\cdot}6$, or $y>1{\cdot}5\,s$. The relation now reduces to

$$\eta = \gamma-\tfrac{1}{2}(p-1)\{\log(p+1)-\log p\}.$$

This shows that the correction to the distance depends only on the ratio of the field-strengths on the two sides of the gauze. When p is large $(\gamma-\eta)$ approaches the limit $\frac{1}{2}$; this means that the travel of the ion is shortened, owing to the openings in the grating, by ·159 of the spacing. As the auxiliary field is increased up to equality with the main field, the shortening of the range decreases to zero, and when $E_1>E_2$, $p<1$, there is an increase in the distance travelled. This increase, $(\eta-\gamma)s/\pi$, approaches infinity for $p=0$, but the approach is so slow that, even when the auxiliary field is 100 times the other, $(\eta-\gamma)$ is only 2·28, *i. e.* the increase in travel of the ion is ·726 of the spacing. If the force E_2 is now reversed in direction and maintained constant for another period T, it is obvious that the ion will not return quite to its original position at the grating, for its motion at the end of the journey will be opposed by the penetrating field. Its final position is given by the equation

$$(p+1)\log(pe^{\eta}-e^{-\eta})-(p-1)\eta = 2p\log p-(p-1)\log(p+1).$$

This cannot be simplified, because it is not now permissible to neglect $e^{-\eta}$. The following values have been calculated :—

E_2/E_1 =	y/s =
·01	·840
·1	·471
1	·153
10	·023
∞	0

Under a continued succession of simple reversals in the field the ions would work their way across any distance. To prevent this, and to ensure that all ions which do not reach the plate are swept back to the gauze, it is usual to make the reversed force greater than the direct. The above figures show that, from the purely electrostatic point of view, a comparatively slight degree of asymmetry in the alternations would be sufficient to secure this. That other considerations must enter into the matter is shown by some results given by J. S. Rogers in a recent paper *. To get definite measurements he found it necessary to make the reverse force greater by 25 per cent., although he was working with a continuous plate instead of gauze.

With the reversed field there will be a plane of zero force near the grating which acts as an impassable barrier to the returning ions. The position of this is given by

$$y/s = -\log p/2\pi.$$

It thus lies on the positive or negative side according as p is less or greater than unity, as is otherwise obvious. Some values are given below :—

$E_2/E_1 =$	$y/s =$
·01	·753
·1	·367
1	0
10	−·367

(2) When the alternating force varies in a simple harmonic manner, $E_2 \sin 2\pi nt$ is to be put for E_2 in the equation of motion. The "undisturbed" distance travelled by an ion during the positive half-period is now $c = kE_2/\pi n$. Let p again represent E_2/E_1 and put $\pi y/s = \eta$, $\pi c/s = \gamma$, $2\pi nt = \xi$. The differential equation is then

$$(4p/\gamma)\, d\eta/d\xi = p \sin \xi(1+\tanh \eta) + (1-\tanh \eta).$$

When the auxiliary field is very weak (p large), this approaches the integrable form :

$$(4/\gamma)\, d\eta/d\xi = \sin \xi(1+\tanh \eta),$$

which leads to the following equation for the value reached by η when $\xi = \pi$, beginning with $\eta = 0$ for $\xi = 0$,

$$\eta - \tfrac{1}{2}e^{-2\eta} = \gamma - \tfrac{1}{2}.$$

As before, the exponential can be neglected, so that, exactly as in the former case, the range is shortened by $s/2\pi = ·159$.

* Phil. Mag. v. p. 888 (May 1928).

For the general case an approximation to the truth can be got by the method of "isoclines". The plane of $(\xi\eta)$ is covered with a family of curves, the loci of points where $d\eta/d\xi$ has a definite value and an integral curve drawn which crosses each of these at the right slope. In the account of this method given by M. d'Ocagne in his 'Calcul Graphique et Nomographie' it is pointed out that a more definite mode of approximation is obtained when the integral curve is built up of pieces of parabolas, with vertical axis, between each pair of isoclines *. He gives a construction by which, when the point on one isocline is known, the corresponding point on the next can be found. This depends on the fact that two tangents to a parabola intersect on a vertical midway between the verticals through the points of contact. A much simpler construction to the same end is provided by another parabolic property. If two tangents to a parabola make with the perpendicular to its axis angles $\tan^{-1}m_1$, $\tan^{-1}m_2$, then it is easily shown that the chord joining their points of contact makes with the same direction the angle $\tan^{-1}\frac{1}{2}(m_1+m_2)$. The desired construction can therefore be quickly carried out by drawing a succession of chords between consecutive isoclines, the tangent of the slope of the chord being the mean of the values belonging to the isoclines †.

In the present case, if we write θ for $(4p/\gamma)\,d\eta/d\xi$, the equation of a isocline is

$$p\sin\xi = (\theta-1+\tanh\eta)\,/\,(1+\tanh\eta).$$

A definite value having been assigned to p, the above curves were drawn, each marked with its θ. This diagram could then be used for any plate-distance; the slopes on the curves being found by dividing θ by the assumed value of $4p/\gamma$.

In practice the axis of ξ was divided in degrees, and this changed the factor $4p/\gamma$ into

$$720p/\pi\gamma = 720sp/\pi^2c = 72{\cdot}97ps/c.$$

To simplify the arithmetic, round numbers were taken for this magnitude, such as would give reasonable values for c/s.

It was not necessary to carry on the construction for the full range of motion. Above the level of $\eta=2{\cdot}5$ to 3 the isoclines run up as vertical straight lines. Once this region is reached the further course of the integral curve is

* *Loc. cit.* p. 156.

† I owe this suggestion, and the carrying out of the work of drawing, to my brother, Mr. F. Morton.

of sine-form and the remaining distance can be calculated. The curved portions of the isoclines could therefore be drawn on a large scale, covering the region in which the disturbing effect of the openings of the grating is felt. If the sine-motion is taken to begin on isocline θ, it is easy to show that the total value of η is got by adding to the height already reached the amount

$$\left\{1+\sqrt{1-\frac{\theta^2}{4p^2}}\right\}\pi c/2s.$$

The ions which reach the greatest distance are no longer those which start at $\xi=0$. When $E_2>E_1$ we must take those which leave the gauze when the combined field there is zero, *i. e.* $\xi=-\sin^{-1}(E_1/E_2)$. For $E_2=E_1$ this becomes $\xi=-90°$, the alternating force has its greatest backward value. For $E_2<E_1$ the greatest range continues to be attained by ions starting at this epoch. The following numerical results have been obtained :—

$E_2=E_1$	$c/s=14{\cdot}6$	$(y-c)/s={\cdot}44$
	$36{\cdot}5$	${\cdot}49$
$E_2=2E_1$	$c/s=14{\cdot}6$	$(y-c)/s={\cdot}66$
	$36{\cdot}5$	${\cdot}07$

The numbers are only rough approximations, for the method is not capable of much accuracy, but they are perhaps sufficient to show that the error is again of the order of the spacing. On the whole, therefore, it appears probable that the interpenetration of the fields is not a source of serious error in the measurements.

I am indebted to Prof. J. J. Nolan for suggesting this investigation and for references to the experimental work.

LXXVII. *Quantum Theory and the Analysis of Observations.* By F. J. Selby, *C.B.E., M.A.* *

THE aim of science is to give a simple description of our perceptions. The description must itself be in terms of perceptions; the field to be described widens as, with various aids, our perceptions are extended.

* Communicated by the Author.

In our description we employ certain conceptions, abstractions, defined more or less accurately in terms of our perceptions. Thus in physics we employ the conceptions length, time, mass, and we say that all physical quantities are measurable in terms of these three conceptions, *i. e.* in terms of certain arbitrary units of length, time, mass.

As we attempt, however, to increase the exactness of the description of our perceptions, of our observations, we find that we cannot define these conceptions with absolute precision. Our unit of length may be the distance between two marks on a bar, but the mark is not a Euclidean line and has indefinite boundaries. We may employ a wave-length of light as our unit, but, as we shall see, this again cannot be precisely defined as an object of perception. Time, likewise, is not susceptible of exact definition as a physical quantity. Mass presents similar difficulties; its very definition, indeed, has always proved somewhat intractable, though the accuracy with which mass can be measured, in terms of an arbitrary unit, is not less high than the accuracy of measurement of time and space.

Einstein has suggested that our observations are mainly of coincidences in time and place. A complete observation of any physical phenomenon involves, however, all the three quantities above mentioned. I will direct attention especially to observations involving, directly or indirectly, the use of the eye; but the statement is true of all observations, with the aid of whatever sense they are made.

In the observation of any natural phenomenon, any "event," we are accustomed to differentiate between three things: the entity, external to ourselves, which is the object of our observations; the means, mechanism, sense organ, by which the observation is made; and the subjective self, mind, consciousness, which receives and records the observation. There is no observation in which these three are not involved; there is no perception in which the relative contributions of the three can be entirely separated. They form a trinity in unity: three incomprehensibles and yet one incomprehensible.

My main aim is to consider the methods of analysis of the more delicate observations of modern physics, in which electrons and protons, waves and radiation are involved. In all such observations the eye, as sense-organ, is directly or indirectly concerned. We may employ intermediate mechanisms, photographic plates, thermopiles, photo-electric cells, electrometers as energy receivers and recorders; but

in our interpretation of intensities, in our energy measurements, we base ourselves on comparisons in which the eye is the ultimate judge. It would be easy to conceive an analysis based on a definition of mass derived, say, from the sense of touch; this would not affect the principles I wish to educe or the main features of my argument.

In these refined observations, where we are reaching the limits of perception, we find that it is no longer possible to maintain the differentiation between the three aspects of our trinity. There is interaction between the observed phenomenon and the observing mechanism; the perception is further conditioned by the limitations which restrict the response of mind and consciousness. Some partial discrimination between subjective and objective may still be possible; complete separation of the three components of the trinity will probably remain for ever beyond human capacity, though we are continually extending our means of observation, and there is no need to be dogmatic. We have enlarged the world of our perceptions, but they still set the boundaries to knowledge.

Let us examine now a simple case of observation to which the foregoing ideas are applicable. I will take the example, of much interest of late years in relation to the quantum theory, of the hydrogen spectrum. We will suppose the radiation from glowing hydrogen gas to be refracted by a prism, the resulting spectrum being observed by the eye. Using the ideas of modern wave mechanics, the energy from the glowing hydrogen, after passing through a narrow slit, is conveyed in wave-groups to the prism; it does not "pass through" the prism, but is dispersed by it, and after both surface and internal losses, due to the prism, travels on in a number of divergent wave-groups to the eye. Let us suppose the eye to be receiving from one selected direction a single sequence of these wave-groups. The energy transferred to the retina—no doubt by resonance, since the loss of energy is small—is seen as a spectrum "line," so called, actually a spectrum band of small width and of a definite brightness. I have, of course, not followed the whole course of events in detail: I have selected the changes on which I wish for the moment to concentrate attention. The theories of Planck and Bohr tell us that these changes are not continuous in character: they take place by discrete amounts, quanta; they are finite changes, brought about by resonance, from one stationary state to another. The transfer of the energy to the retina is one of these changes and

of the same nature as the rest: it takes place by quanta. But let us examine the phenomenon from the receiving end; consider its aspect from the point of view of the eye and the conscious mind behind it. It would be in accord with our general experience to suppose that there is a *minimum sensibile*, a minimum disturbance below which no effect is produced on the consciousness; a minimum change, also, which is perceptible, which may (or may not) be of identical amount. The eye receives a succession of wave-groups associated with a certain frequency, the group or beat frequency: it responds by resonance, after a very brief interval: the natural measure of the response is therefore of dimensions energy × time, *i. e* of action. Let us suppose that there is a certain minimum of response, the quantum of action, which is perceptible by the eye and the mind behind it. We can now trace back our phenomenon to its objective end, but we must retain our quantum of action as an indivisible unit. We realize at once the reason for the appearance of the quantum in all visual phenomena; it is inherent in ourselves. Planck's constant h, Bohr's quantum of action, cannot but be identical with it *, since any transfer of energy to the eye as a receiving mechanism will be governed by the usual quantum laws. Indeed, it is difficult to suppose that there could be two independent quanta involved in phenomena.

Let us continue our analysis. Reception by the eye of the light from the single hydrogen "line" is associated with a definite frequency, the group or beat frequency. The eye is comparable with a heterodyne receiver, capable of responding over a certain range of frequencies; the range is no doubt different for different eyes, as the range of audibility is different for different ears. The group frequency is related to the wave frequency by the Rayleigh formula. If we denote the energy received in the usual manner by $\int I d\lambda$, we realize that the wave-length is a conception, an abstraction, merely; it is one of the boundaries of an integral field. But it is clear that we can think in terms of the ordinary wave theory; and the conclusions reached with the aid of that theory hold good. We note, in passing, that the wave-group has no definite boundaries: it dies away rapidly from a maximum, but may be supposed to extend to infinity in either direction: a succession of

* We can conceive that the *minimum sensibile* may be a submultiple of h, but there would appear to be no means of perceiving such a distinction.

wave-groups is a succession of maxima, of singularities, in a wave-field.

In considering next the dispersion of the hydrogen light by the prism, we can adopt the usual wave theory; but we must bear in mind in our analysis that we are dealing with indivisible quanta of action, and frame our conceptions accordingly. The transfers of energy which take place again occur by resonance.

Tracing our phenomenon further back to the radiating atom, we have the option of treating it by the methods of particle mechanics, or by the new methods of wave mechanics. We must, however, recognize that our particle is comparable with the wave-group, the singularity in a wave-field, and has no definite boundaries. Newton's corpuscular theory of light and the wave theory combine to form a more comprehensive whole.

Let us return to the ideas with which we started. To describe our perception of an event, we make use of three conceptions—length, time, and mass; or we may say length, time, and action. There is a natural, indivisible, unit of action, the quantum. Expressed in terms of mass, the dimensions of this quantum are MV^2T or MVL, where V is velocity, of dimensions L/T. If, now, we choose arbitrary units of mass and length, say the mass of the electron and the wave-length of the red cadmium line, there is a corresponding definite value of V which is not infinite; we must not suppose V to become infinite without at the same time supposing M or L to become infinitely small. We are, in fact, dealing with a "complementarity," to use Bohr's term with a somewhat different significance, a trinity in unity, and we must adjust our conceptions accordingly. We thus reach what we may call an extended theory of relativity, which includes quantum theory, in which length, time, and mass are inter-related and the quantum of action is an invariant.

Let us now suppose that in the observation of any phenomenon we wish to follow the changes of some quantity Φ. Our quantum, wave-group, electron or proton is capable of motion in three directions and of rotation about three axes in space. Let its position or configuration at any instant be determined by the variables $x, y, z, \theta, \phi, \psi$. Other variables involved are t and nh, where n, however, must be an integer, h being Planck's constant, the quantum of action. Our quantity Φ is a function of these variables:

$$\Phi(x, y, z, \theta, \phi, \psi, t, nh).$$

Experience indicates that, as a first approximation in considering the changes of Φ, we can neglect differential coefficients of higher order than the second. The changes will thus be given by a differential equation of the form

$$f_{rs}\frac{\partial^2\Phi}{\partial\xi_r\partial\xi_s}+f_r\frac{\partial\Phi}{\partial\xi_r}+f_0=0,$$

where ξ denotes any one of the variables and the f's are functions of any or all of the variables *. Our procedure is to try to fit solutions of this equation to the phenomena, remembering that n can only change by integral steps.

Various methods of obtaining solutions of this equation in particular cases have been devised by Bohr, Heisenberg, Schrödinger, de Broglie, Dirac, and others, and remain applicable without modification with the conceptions introduced above. It is very instructive to realize how the experimenter, by inductive reasoning, has been led to introduce into his conceptions, in order to explain observed phenomena, the "subjective" unit, the quantum, which was unavoidably involved in the limitations of his powers of perception.

I do not propose to follow my subject further in the present note. Much no doubt remains to be done in the devising of rapid methods of calculation applicable in the analysis of observations of the kind to which attention has been devoted, but already good progress has been made. It is hoped that the foregoing may assist the physicist who has not acquired the mathematical technique to grasp at least the *rationale* of the procedure which is being followed. He will find much further information in Bohr's article published in 'Nature' on April 14th, to which this note may be regarded as a corollary.

I have been concerned with microscopic or, I might say, sub-microscopic phenomena. In dealing with macroscopic or statistical phenomena we can employ the usual procedure; it is only at the surfaces of bodies, or at the boundaries of our field, that we may need to resort to the more complicated technique of the new methods.

* Repetition of suffixes implies summation, as in relativity notation.

May 28th, 1928.

LXXVIII. *The Continuous Spectrum of Hydrogen.*

By F. H. Newman, *D.Sc., F.Inst.P., Professor of Physics, University College of the South-West of England, Exeter* *.

[Plate XIII.]

1. *Introduction.*

THE origin and exact character of the continuous spectrum of hydrogen, which has been investigated by many observers, still remains uncertain. In some cases this type of spectrum possesses the peculiar characteristic of occurring without the presence of either atomic or molecular lines, and an explanation of this fact has been advanced by Kaplan †, who suggests that when the hydrogen molecule in the first electronic state possesses more than 0·50 volt vibrational energy, it may split into two atoms with emission of energy as radiation, the value 0·50 volt being derived from the observed short wave-length limit of this continuous spectrum. The absence of observed lines is due to the fact that transitions from the initial excited state of the molecule to lower ones give rise to lines lying far down in the ultra-violet region.

This spectrum, which is quite distinct from that one which begins at the limit of the Balmer series and continues towards the shorter wave-lengths, appears in celestial spectra in the absence of the Balmer lines and the secondary spectrum, and its limit on the red side is always at wave-lengths greater than λ 3646 ; for example, as an absorption spectrum it begins in α Cygni at λ 3710, having a maximum intensity at λ 3660, approximately, and in Vega it commences at λ 3800, its maximum being at about λ 3710.

Crew and Hulburt ‡ found this type of spectrum to be of similar character, although of differing intensity, in a number of sources, including a long hydrogen tube constructed after the manner of Wood with the light coming end-on through a quartz window from the central portion only, an ordinary discharge-tube, the separate striations of the positive column, the condensed spark in hydrogen at pressures above atmospheric, and in the water spark. In all cases it was of appreciable intensity near Hα, rising slowly to a maximum in the rear ultra-violet, and descending slowly in intensity from λ 3000 to λ 2200.

* Communicated by the Author.

† Nat. Acad. Sci. Proc. xiii. p. 760 (1927).

‡ Phys. Rev. xxviii. p. 936 (1926).

Adopting Bohr's theory, a continuous spectrum extending into the ultra-violet should begin at the limit of the Balmer series, λ 3646, and it may be noted that Herzberg *, using the electrodeless ring discharge in hydrogen, has obtained this type of spectrum, the intensity variation in the continuum being continuous with that in the Balmer series. The wave-number at the beginning of this spectrum corresponds to the energy set free in the fall of an electron from rest at infinity into the second orbit. If such an electron possesses additional energy of its own, it gives up more energy when it is bound than one at rest, and this energy appears as radiation of wave-length less than that corresponding to the Balmer series limit. Since the initial kinetic energy of the electrons, external to the atom, varies from one electron to another, it is evident that the resulting radiations constitute the continuous spectrum beginning at the limit of the Balmer series and extending towards the ultra-violet. This theory is based on the assumption that the atomic orbits extend to infinity; but originally it was supposed that the size of the orbit system is restricted by the density of the radiating gas, and from this Wright † has inferred that it is necessary to substitute for the orbit at infinity the largest orbit in effective operation. Into this orbit, therefore, will enter electrons of all energies from zero upward. An electron thus entering the effective orbit and having zero initial kinetic energy will, on transfer to the second orbit, give rise to radiation of wave-length which forms the limit of the continuous spectrum on the red side; and it is to be expected, therefore, that the continuous spectrum would begin somewhere on the less refrangible side of the last visible line in the Balmer series, and that there should be an overlapping of this series and the continuous spectrum. As Nicholson ‡ has pointed out, however, numerous experiments now show that the number of lines in the Balmer series available for observation is not determined necessarily by the density of the gas; and he cites his experiments made in conjunction with Merton §, in which they observed fourteen sharp lines of the series in a tube filled mainly with helium at 42 mm. of mercury pressure, such that the radius of the hydrogen atom emitting the last member on this Bohr theory was twice the average distance apart of the atoms. Wood's experiments with long

* *Phys. Zeits.* xxviii. p. 727 (1927).
† 'Nature,' cix. p. 810 (1922).
‡ Roy. Astron. Soc. Monthly Notices, lxxxv. p. 253 (1925).
§ Proc. Roy. Soc. A, xcvi. p. 116 (1919).

discharge-tubes also preclude any correspondence between the number of lines visible and the density of the gas.

Nicholson supposed that this spectrum arises from the actual binding of stray electrons by the atoms, the electron having any kinetic energy in excess of that required for its motion in the path of the atom which it enters, the excess being emitted as radiation, so that the wave-numbers of the resulting radiation will form a continuous set, giving rise to a continuous spectrum. If the law of the distribution of velocity among these electrons which are thus captured is that deducible from the kinetic theory, the law of intensity throughout this continuous spectrum can be calculated and compared with that found experimentally. Crew and Hulburt * calculated this energy distribution by statistical methods, and found that the relative intensity involves an unknown probability, a_n, that the atom exists through the nth orbit, the region beyond being unquantized. When a_n is evaluated, approximately, from general physical considerations, the formula agrees qualitatively with the relative intensity throughout the spectrum obtained from the hydrogen stars and laboratory sources.

2. *Experimental.*

The author has found another method by which this continuous spectrum may be produced at very low pressures, viz. by means of the electric arc passed between cold electrodes in a rarefied hydrogen atmosphere. An intermittent electrical discharge is passed between two iron electrodes in a discharge-tube, and between one of these electrodes and a third one a potential difference of 200 volts is applied continuously. The tube contains hydrogen at a pressure of 10^{-3} mm. of mercury, and on passing the electrical discharge an arc through the gas may be produced. The resulting radiation shows no trace of iron lines, provided that the arc is allowed to continue for a few seconds only, otherwise owing to the heavy current through the gas, which may amount to 10 or more amperes, the electrodes quickly reach a sufficiently high temperature to emit the ordinary iron arc lines. The radiation emitted, which is pale blue or whitish in colour, has been examined and photographed through a quartz window by means of a quartz spectrograph. It has been found that the resulting spectrum varies according to the condition of the gas ; but in all cases, and in spite of the low pressure, only a few of the Balmer lines actually

* *Loc. cit.*

appeared, those of wave-length shorter than H_δ not being visible on the photographic plates.

If the hydrogen was not dried, the water bands, particularly those at $\lambda 3064$ and $\lambda 2811$, were prominent together with a few Balmer lines, but there was no continuous spectrum. On the other hand, when the gas was dry the water bands were absent and the continuous spectrum became very marked, being accompanied by the secondary hydrogen lines. It was difficult to estimate with any degree of exactness the limit of this continuous spectrum on the red side; but the average value of this limit, taken from numerous spectrograms of various exposures, gave the value $\lambda 4690$, approximately, the last line of the Balmer series which could be detected on the plates being H_δ, $\lambda 4102$. Thus, if ν_1, ν_2, ν_3 represent the wave-numbers of the limit of the continuous spectrum on the red side, the limit of the Balmer series and the last detectable line of this series, respectively,

$$\nu_3 - \nu_1 = \nu_2 - \nu_3,$$

or

$$24373 - 21320 = 27420 - 24373,$$

$$3053 = 3047.$$

Although these numbers are only approximate, the result suggests that the margin of overlap of this continuous spectrum and the last observed Balmer line is equal to the interval between this line and the theoretical limit of the series. This supports Wright's view of the phenomenon; but it must be remembered that on the whole comparatively few electrons of approximately zero velocity are to be expected on the kinetic theory, and as these determine the limit at the red end of the spectrum, this limit will necessarily be ill-defined.

An interesting feature of the spectrograms is the effect of water-vapour on the appearance of this continuous spectrum. If the water bands are prominent the continuous spectrum is absent, as shown at I. (Pl. XIII.), whereas it becomes more and more intense as the bands disappear (II., Pl. XIII.).

The continuous spectrum may not arise from the interaction of an electron with the nucleus of a free atom: the atom may be influenced directly by other atoms or ions; for example, it may arise from the molecules, and Herzberg * suggests that the experimental conditions of excitation accord best with the view that the breaking-up of molecular ions H_2^+ is the cause.

* *Loc. cit.*

The present experiments show that association of water molecules with the hydrogen atoms and molecules opposes the continuous spectrum excitation, and suggests that it is associated with the atoms, and certainly not with molecular aggregates. It must be noted, however, that this does not necessarily mean that the hydrogen molecules are ineffective in the emission. The restricted outer orbits may be part of a molecule.

In connexion with this type of spectrum, there is the case of iodine in which an emission spectrum has been photographed by Steubing * and which appears as a continuous band, even at the highest resolution. Franck † has explained this from the electro-negative behaviour of the iodine atom with its tendency to perfect itself into an eight-shell by taking up an external electron, but in this case the iodine atom need not be ionized to attract the foreign electron; the electron affinity suffices to effect the assimilation of the foreign electron, even in the case of the neutral iodine atom. In this phenomenon the continuous character of the spectrum also corresponds to the continuous distribution of the initial kinetic energy of the assimilated electron.

LXXIX. *The Electric Arc in Gases at Low Pressures.* *By* F. H. Newman, *D.Sc., F.Inst.P., Professor of Physics, University College of the South-West of England, Exeter* ‡

1. *Introduction.*

A NEW type of electric arc in high vacua has been described by the author § in which with cold electrodes an arc could be started and maintained in various gases at very low pressures, provided that an initial electrical discharge was passed between one of the "arc" electrodes and a third electrode placed within the discharge-tube. There were two separate effects: first the ordinary arc in which the current reached 10–15 amperes, and secondly a brilliant glow discharge during which a very small current passed through the tube. Both of these effects could be excited at such low gas-pressures that there was practically

* *Zeits. f. Phys.* v. p. 428 (1921).
† *Ann. d. Phys.* lxiv. p. 693 (1921).
‡ Communicated by the Author.
§ Phil. Mag. ii. p. 796 (1926).

no luminosity due to the electrical discharge. Later, Ratner * observed a very similar arc carrying many amperes which could be maintained in a vacuum as high as 10^{-3} mm. of mercury. For example, he found that at 10^{-3} mm. pressure a potential difference of 60 volts was sufficient to start the arc, at 5×10^{-2} mm. 120 volts was necessary, while at 1 mm. pressure a potential difference of 230 volts was not sufficient. It is evident, however, that the requisite voltage not only depends upon the gas-pressure, but also upon the distance between the electrodes. The latter may be of any metal, and the arc shows the usual current voltage characteristics. In some respects it is unilateral in that the polarity of the arc must bear some relationship to the polarity of the auxiliary electrical discharge, the arc only passing if the electric fields are in the same direction. Ratner has also found a similar unilateral relationship, although he noted, in addition, that the arc strikes independently of the direction of the field between the two "arc" electrodes when the third electrode, which is concerned solely with the electrical discharge, is the anode.

The formation of such an arc, passing practically unlimited currents, is interesting and surprising because the very low pressure in the tube made it almost impossible for the discharge to pass, and there was no sign of luminosity, the tube walls fluorescing under the cathode ray action. Occasionally a brilliant white glow was formed between the "arc" electrodes, but it was a momentary effect, existing prior to the starting of the arc proper. During this glow the electrodes remained cold, the actual current passing being but a small fraction of an ampere.

These effects indicate that the mechanism of the arc is entirely different from that of the ordinary electrical discharge, and further investigations on the actual conditions necessary for this arc to be started have been made.

2. *Experiments.*

The actual apparatus used was similar to that described in the previous paper, and although the effects can be produced with any type of metallic electrodes, iron rods were employed in all the experiments, chiefly because thick rods of this metal were available. With such heavy currents as were passing, these electrodes became very hot after the current had been flowing for a short time-interval, and finally it was found necessary to water-cool the electrodes to prevent the

* 'Nature,' cxx. p. 548 (1927).

wax, by means of which they were sealed into the discharge-tube, from softening. Another difficulty, due to the intense heat generated, was the liberation of gas from the walls of the vessel and from the electrodes with resultant increase of pressure within the vessel. To overcome this a large reservoir was sealed to the tube so that this gas emitted did not materially change the pressure in the apparatus while the arc was passing.

When the arc was first started the radiation emitted was entirely that from the gas molecules within the vessel, but the electrodes rapidly became red-hot and the characteristic radiation from the iron quickly made its appearance, the electrodes then becoming incandescent. As a rule, however, the arc was allowed to persist only for a short interval, as, once started, it is easily maintained, and it is the actual process of striking that is interesting and worthy of study. In passing, it may be noted that this method is very convenient and useful for starting and maintaining an iron arc in a very high vacuum, if it is desired to study the iron lines *in vacuo*.

The lowest applied potential difference with which it was possible to strike the arc was 108 volts, but it started most consistently at 200 volts, and the current which could be passed varied from 0·4 ampere upwards. Below this limiting value it was impossible to maintain the arc. Another factor which greatly influenced the process of starting was the type of electrical discharge employed. If the latter was feeble it was ineffective. A momentary discharge produced by temporarily switching in the induction coil commutator proved to be the best means of starting the arc. Thus a very high potential difference from the coil is necessary, and the most consistent results were obtained when the secondary discharge was unidirectional. The arc would not strike at pressures above 10 mm. of mercury, and worked better at lower pressures, particularly those within the range 10^{-2}–10^{-3} mm.

In order that the arc may occur, the gas present must be ionized, and for this energy is required. This comes from electrified bodies which have acquired high velocities under the electric force from the transient electrical discharges, the initiation of the latter being due to stray electrons or electrified atoms, particularly to stray electrons. Before these electrons can ionize the gas, a time must elapse which is large in comparison with the time-interval between one collision of the electron with a molecule of the gas and the next, since before the electron can ionize it must obtain from the electric

field energy greater than the ionizing potential of the gas, and this energy must be conveyed to an electron in a molecule before an electron can be liberated. Thus there is produced a fairly copious supply of electrons which, under the further influence of the field due to the applied potential difference, form more ions by collisions, provided that the mean free path of the electrons is so large that they attain energy equivalent to the ionizing potential of the gas through which the electric arc passes. It seems, therefore, that the function of the electrical discharge is to provide those electrons which are ordinarily supplied by the incandescent electrode of the ordinary arc, or by the incandescent filament of a low-voltage arc.

In connexion with the initial ionization in a gas, Sir J. J. Thomson * has given an account of experiments on the radiations inside a closed vessel containing gas at a low pressure through which an electrical discharge is passed. These experiments indicate that the passage of the electrons through gases gives rise to Röntgen rays which may be of far higher frequency than any of the characteristic radiation of the gas. For example, he finds that, when electrons formed by a potential difference of 1500 volts are sent through hydrogen, Röntgen radiations having a frequency corresponding to 1500 volts were detected. The type of radiation at constant pressure depends upon the means used to send the discharge through the tube ; for example, it depends upon the nature of the interrupter and its working. This is to be expected, as the potential difference between the electrodes often depends upon the nature of the discharge.

In addition, some of the radiation within the discharge-tube is of an exceedingly absorbable type, so absorbable that it is practically stopped by the equivalent in mass of a layer of air a few millimetres thick at atmospheric pressure. He supposes that this soft radiation produces the ionization in the negative glow.

At the lower gas-pressures the electrons, owing to their greater mean free path, have large amounts of energy, and they give radiations over a larger range of frequency than those with smaller amounts, although the density of the energy is not so great. At each collision the fast electrons may not produce much more radiant energy than the slow ones, but they are able to make many collisions with atoms and molecules before their energy is so

* Phil. Mag. xlix. p. 761 (1925).

much reduced that they are unable to generate Röntgen radiation. Hence the total amount of radiant energy produced by a fast electron will be much greater than that formed by a slow one, with the resultant increased ionizing effects. Thus we should expect a greater concentration of the electrons at the lower pressures; and this explains why the arc in the present experiments can be started more easily and consistently as the pressure is reduced. As Thomson * has shown, the radiation from the cathode rays is a mixture of soft radiation with quanta represented by a few volts, together with much harder radiation whose quanta may be comparable with a hundred volts. In addition there is the softer type of radiation produced by the positive rays. Seeliger † has shown that the total number of ions produced by a positive ray does not vary much either with the speed of the ray or with the gas-pressure; and this suggests that the ionization is due, not to the energy of translation of the particle, but to energy internal to it, such as might be represented by supposing the particle to contain a limited number of undischarged radiation quanta. These excite the ionization. The experiments made by Thomson ‡ on the electrodeless ring discharge show the existence of such radiations of wave-lengths shorter than those of visible light.

3. *The Effects of Foreign Bodies on the Arc.*

After the arc electrodes had been used for some time, it was impossible to start the arc, and on examining the electrodes they were found to be coated with a film of oxide arising from the decomposition of carbon-monoxide and carbon-dioxide gases, which are very difficult to remove from the vessel. If the electrodes were withdrawn and scraped, the arc could be produced as before. On the other hand, it was found that when patches of fused salts, such as potash, soda, sodium chloride, and calcium carbonate, were placed at the ends of the electrodes, the arc would strike more readily and consistently, this effect being, in fact, the reverse to that produced by the film of oxide on the metal. In addition, it was noted that usually a brilliant spot appeared on the cathode, even in the absence of any fused salt, and that this spot continuously changed its position, as it does in the mercury arc.

The effect of the fused salts can be explained by an

* Phil. Mag. ii. p. 674 (1926).
† *Phys. Zeits.* xii. p. 839 (1912).
‡ *Loc. cit.*

abnormal local heating, brought about by the bombardment with the positive ions. The salt, or a small part of it, is raised to incandescence, with the result that it emits a copious supply of electrons; and we have, therefore, a thermionic source similar to that of an incandescent cathode, only on a small scale. As a result the starting of the arc is facilitated. As opposed to this effect, the oxide film prevents these positive ions from bombarding the cathode, and, accordingly, there is no local heating-effect at the small particles of impurities, which exist even in the purest of iron. Thus the arc cannot be started.

These experiments seem to prove conclusively that this phenomenon of the cold electrode arc is due mainly to the localized heating-effect at these foreign particles which gives a copious supply of electrons from such local sources. Anything that shortens the life of the electron will increase the difficulty of getting the arc, but anything that reduces the number of collisions, required by one electron to detach another from a molecule, will facilitate the arc starting. It has been found that a thin deposit of sulphur is formed on the walls of the discharge-tube after the experiments have been continued for some time, this sulphur coming from the iron electrodes. Now, sulphur is very strongly electronegative, and, presumably, a sulphur molecule would be likely to capture an electron in collision, so that, although the vapour-pressure of sulphur is exceedingly low, the presence of this element would diminish the life of the electrons. The various gases present in the tube, such as nitrogen, hydrogen, etc., combine with the sulphur, and if these products, like sulphur, possess the power of capturing electrons, then the ionization in the tube is decreased, and this precludes the starting of the arc. On the other hand, complexes formed by aggregation, such as are produced by traces of moisture, facilitate the production of the arc. This may be explained by the electron detaching an electron more easily from one of these aggregates than from a single molecule. The moisture appears to act as a catalyst for the arc as it does in many cases of chemical combination. The existence of these aggregates is suggested by some experiments of Thomson *. The ordinary electrical discharge through gases produces also other modifications of the gases which only persist for a short time. In some cases, for example, with nitrogen and oxygen the existence of these modified forms is shown by the visible after-glows. We also

* Phil. Mag. iv. p. 1128 (1927).

know that the discharge and the arc can be maintained with lower applied potential differences than those required to start them, and this fact can be explained by the discharge and arc producing systems which are more easily ionized than the normal molecules.

It is evident, therefore, that in the present experiments the initial electrical discharge gives rise to two effects which facilitate the starting of the arc. In the first place it produces intense local heating of impurities lying on the surface of the cathode with resulting thermionic emission, and in the second place modifications of the gas arise, these modifications being more easily ionized than the gas in the normal state.

LXXX. *The Motions of Electrons in Ethylene.* *By* J. Bannon, *B.Sc.*, *and* H. L. Brose, *M.A.*, *D.Phil.*, *F.Inst.P.* *.

IN an address given by Professor Townsend at the centenary celebration of the Franklin Institute in Philadelphia, September 1924, the type of instrument used in the present research has been fully described. The instrument affords a ready and accurate means of determining the velocity W in the direction of the electric force, and the velocity of agitation U of electrons in gases. It has been found that in nitrogen, hydrogen, and oxygen †, amongst other gases, these velocities depend only on the ratio of the electric force Z to the gas pressure p. A similar result has been obtained for ethylene, especially for values of Z/p greater than 5. Exceptionally tedious was the work on this gas, which appeared to alter as a result of making observations. This alteration manifested itself solely as an increase both in W and U.

In Table I. the values of Z and p, with the corresponding values of k and W, are given, where k represents the ratio of the mean kinetic energy of agitation of an electron to the mean kinetic energy of a molecule of a gas at 15° C. The numbers given are the means of several experiments, which are in good agreement. For values of Z/p, equal to

* Communicated by Prof. J. S. Townsend, F.R.S.

† J. S. Townsend & V. A. Bailey, Phil. Mag. xlii. p. 875 (Dec. 1921); H. L. Brose, Phil. Mag. l. p. 543 (1925).

and less than 5, the values of k increase appreciably as the pressure is reduced. This indicates the presence of some ions at the higher pressures, for, within any particular region of relative velocities of electrons and molecules, the number of ions formed is a function of the number of collisions. A direct method of testing for ions, used by Townsend and Bailey, is to apply a horizontal magnetic field of intensity about ten times that necessary for the determination of W. In the case of ethylene, for Z/p equal to 1·26, such a field sufficed to deflect about 90 per cent. of

TABLE I.

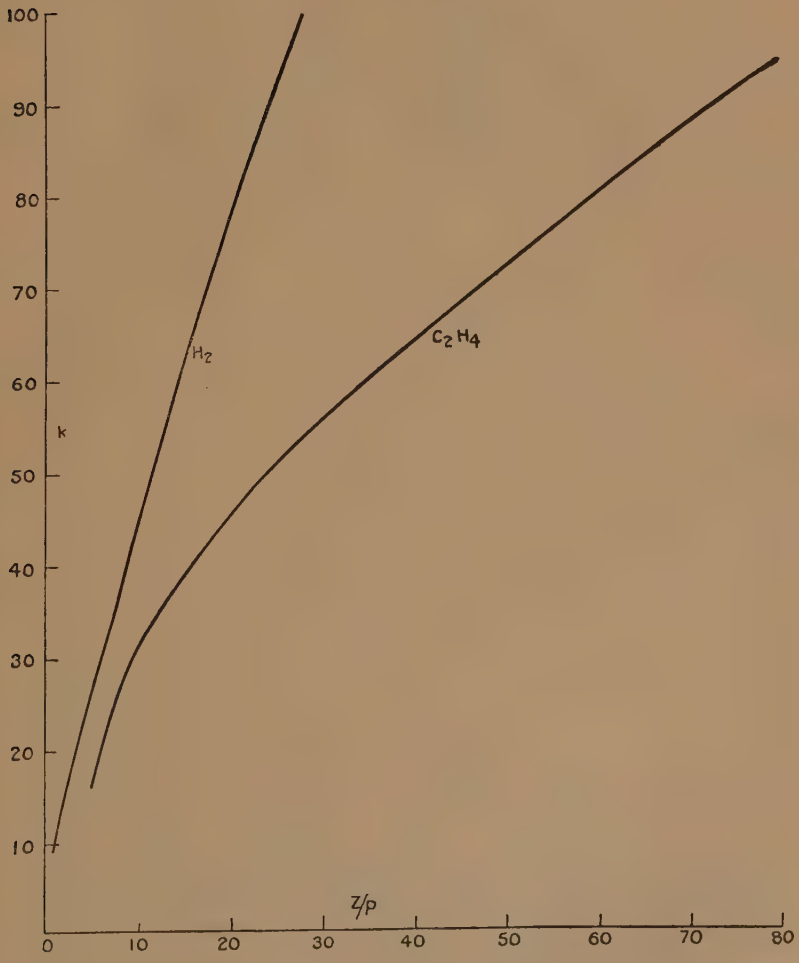
Z/p.	Z. volts per cm.	p. mm.	k.	$W \times 10^{-5}$. cm. per sec.
1·26	4·88	3·87	2·07	23·3
2·47	9·52	3·86	4·51	39·5
2·53	4·90	1·94	5·70	38·8
5·03	19·56	3·89	13·5	50·5
4·95	9·65	1·94	15·4	53·3
5·00	4·85	·97	16·25	55·2
10·1	38·8	3·86	28·7	58·5
10·2	18·9	1·85	30·1	59·8
10·1	9·7	·96	32·5	62·2
20·2	39·1	1·93	43·8	64·8
20·1	19·3	·96	45·9	68·3
20·1	9·55	·475	45·5	67·8
40·3	38·7	·96	64·5	89·2
40·0	19·0	·475	63·4	87·8
49·9	23·7	·475	71·8	103·3
80·0	38·0	·475	95·0	144·5

the electric charge on to one of the outer electrodes, and at least 98 per cent. for Z/p equal to 80. Hence, even for the lowest ratio of electric force to pressure the current was due almost entirely to free electrons. The magnetic field acts as an analyser, separating the comparatively slowly-moving, massive ions, which suffer little deflexion, from the small rapidly-moving electrons. As ions were beginning to make themselves evident, and as k was approaching unity, measurements were not made below the value 1·26 for Z/p.

The curves given in figs. 1 and 2 represent the values of k and W for various values of Z/p. For the sake of com-

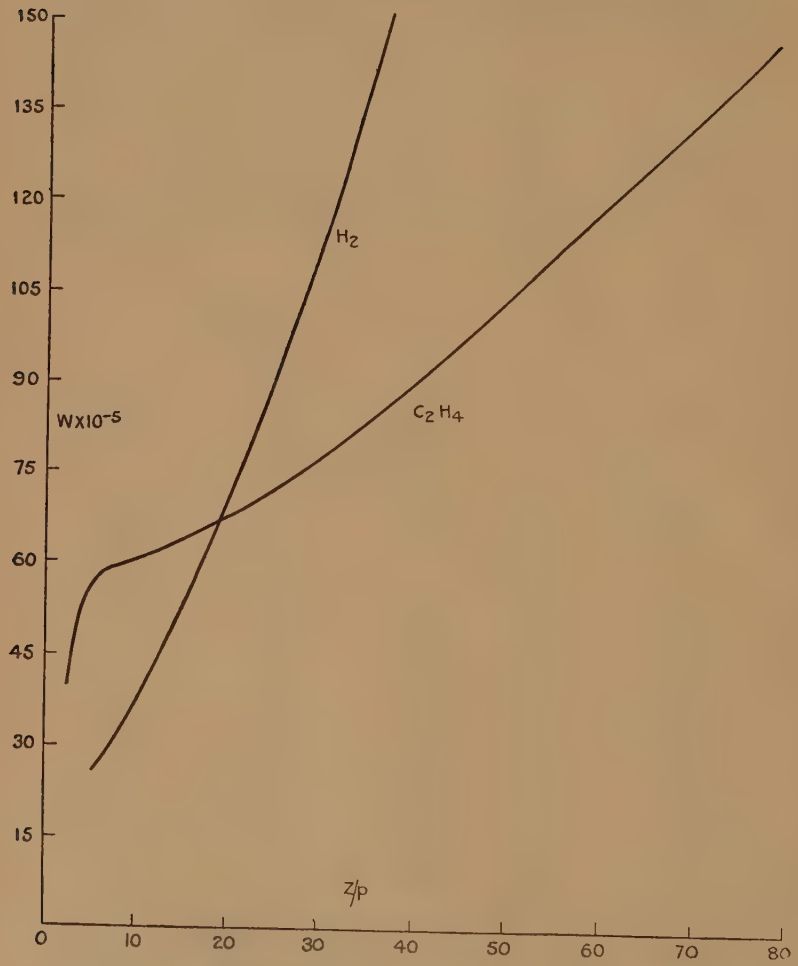
parison the curves for hydrogen and oxygen are inserted. The values of k and W, as read from the ethylene curves, for the various values of Z/p are given in the first three

Fig. 1.



columns of Table II. In the other three columns are given the values of U, the root mean square velocity of agitation of an electron, L, the mean free path of an electron in the gas at 1 mm. pressure, and λ, the fraction of the mean kinetic

Fig. 2.



energy of an electron lost in a collision with a gas molecule. U, L, and λ are calculated from the formulæ

$$U = 1{\cdot}15 \times 10^7 \sqrt{k},$$

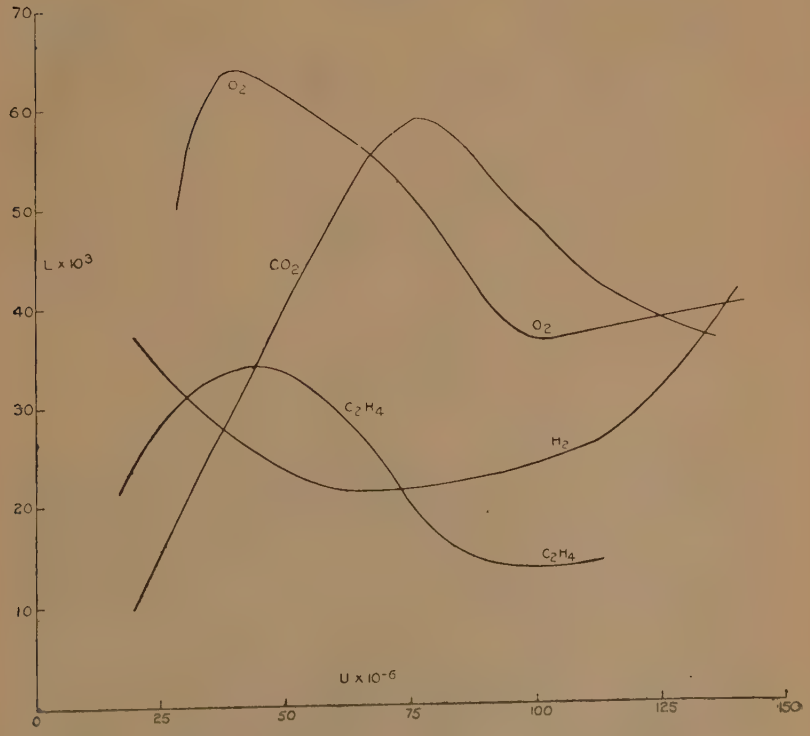
$$W = {\cdot}815\ Z/p \times \frac{e}{m} \times \frac{L}{U},$$

$$\lambda = 2{\cdot}46 \frac{W^2}{U^2}.$$

TABLE II.

Z/p.	k.	$W\times10^{-6}$. cm./sec.	$U\times10^{-6}$. cm./sec.	$L\times10^{2}$. cm.	$\lambda\times10^{4}$.
1·26	2·07	23·3	16·6	2·14	488
2·5	5·3	39·3	26·5	2·92	541
4	11·0	49·6	38·1	3·28	416
5	15·0	54·0	45·3	3·42	348
6	19·3	56·0	50·5	3·30	303
10	31·3	60·3	64·3	2·71	217
20	45·3	67·6	77·4	1·83	187
40	64·4	88·7	92·3	1·43	227
60	80·2	116	102	1·38	319
80	95·0	145	112	1·42	408

Fig. 3.



For ethylene, the variation of L with U is shown very strikingly in fig. 3. This curve, like the curves of oxygen and carbon dioxide, has a very definite maximum, with a less definite minimum.

From the sixth column of Table II. it is seen that the percentage energy lost by an electron in collision varies for the most part between 2 and 5. The minimum fraction of energy is lost by the electron when its agitational velocity is in the region of 77×10^6 cm. per sec., which is equivalent to the volt-velocity 1·7.

The acquisition of new properties by the gas, either as the result of exposure to ultra-violet light or of collisions with electrons (with or without an electric field), was the outstanding difficulty which presented itself. The extent of the change is indicated by data given in Table III. The results are set down in the order in which observations

TABLE III.

Sample.	Date.	Z/*p*.	*p*.	*k*.	W×10⁻⁵. cm./sec.
(*a*)	23rd May, 1927	5	·97	16·3	54·8
		40	·97	64·75	89·5
		5·1	·955	19·4	
	24th May, 1927	5·1	·95	20·2	59·1
		40·3	·95	68·9	91·0
	25th May, 1927	5·2	·94	23·3	62·0
		40·0	·936	71·0	98·2
(*b*)	30th May, 1927	20·3	1·88	44·4	64·1
		2·6	1·88	12·25	40·0
(*c*)	7th April, 1928	10·2	·95	34·2	
		5·1	·95	23·5	
(*d*)	9th March, 1928	10·0	1·06	34·8	
		5·1	1·06	23·4	

were made. For sample (*a*) the first two measurements of *k* for the ratios Z/*p* equal to 5 and 40 respectively are quite in keeping with those shown in Table I. The third, which followed immediately, shows a large increase of *k* for a Z/*p* equal to 5·1. Further increases in the values of *k* are recorded on the following day, and on the third day *k* has reached the value 23·3 for the ratio 5·2 and 71 for the ratio 40. A steady increase in the values of W is also noticeable. For sample (*b*) the first reading gives a value of *k* for Z/*p* equal to 20·3 in accordance with Table I. The reading for the ratio 2·6, however, is more than double that to be expected. The four readings for sample (*b*) were taken within the same hour. Similar remarks apply to (*c*) and (*d*) as to (*b*).

For the purpose of obtaining trustworthy results for ethylene, it was necessary to renew the gas in the instrument

about every three hours, and to make observations from the lowest value of Z/p upwards. To check the accuracy of values obtained in this way the following method of procedure was adopted. The instrument was thoroughly exhausted and, say, 4 mm. of gas were admitted. Readings for k and W were rapidly taken for Z/p equal to 1·26, the instrument was again exhausted, and fresh gas admitted at 4 mm. pressure. This time the ratio was made 2·5. Under similar conditions readings for all other ratios were obtained.

A second difficulty arose from contamination of the reflector used in focussing the ultra-violet light on the copper target. It was necessary to clean it about once every three days, when using the instrument at the rate of six hours a day. That ethylene was responsible there can scarcely be a doubt, because (*a*) the effect never occurred when either hydrogen or pentane was used, and (*b*) the effect was not experienced in working with either hydrogen or ammonia in a second instrument having a reflector made from exactly the same materials in the same workshop.

Both difficulties seem to have arisen, therefore, as a result of the nature of ethylene. The amount of polymerization was negligible, as the decrease in pressure of the gas in the instrument was not more than one per cent. per day. If the molecule decomposed, it could not do so in a way to give free hydrogen, as there would then be a marked increase in pressure. But if the molecule lost one carbon atom, and changed into the saturated hydro-carbon methane, this would account for the variation in k and W, for the contamination of the reflector, and for the fact that the pressure of any particular quantity of gas never increased. The slight decrease in pressure noticed throughout the work was traced to the drying agent phosphorus pentoxide, which absorbs ethylene at the pressures of the experiments and parts with it again when the pressure is reduced.

Estimations based on the electron currents used, the drift and agitational velocities, and the mean free paths show that electron collisions may account for slow changes in the values of k and W for any fixed value of Z/p, but not for the rapid changes observed to occur in one or two hours. Hence the view that ultra-violet light—with perhaps the help of an electric field—may cause rapid change appears tenable.

The electron currents used were of the order 10^{-12} ampere.

The ethylene used in the above experiments was generated by dropping ethyl alcohol into a flask highly exhausted of

air, and containing orthophosphoric acid at a temperature of about 230° C. Oils and other impurities such as alcohol vapour were extracted by passing the gas into traps maintained at the temperature of carbon dioxide snow. A solution of $Na_2S_2O_3$ served the purpose of extracting traces of oxygen. Bubbling through sulphuric acid helped in part to dry the gas, which, after it had passed over phosphorus pentoxide, was finally stored in flasks containing the same drying agent. In the generating and purifying processes the apparatus used was made entirely of glass. Different samples of gas were prepared, and the results from all were in good agreement.

We wish to express our warm thanks to Prof. V. A. Bailey for valuable assistance during the course of the work.

Physics Department,
University of Sydney.

LXXXI. *On the Best Correction Factors for Harmonic Coefficients.* *By* Albert Eagle, *B.Sc., Lecturer in Mathematics in the Victoria University of Manchester* *.

CORRESPONDENCE in connexion with my paper, "On the Relations between the Fourier Constants of a Periodic Function and the Coefficients determined by Harmonic Analysis," in the Philosophical Magazine (Jan. 1928, p. 113) makes it desirable to add a few words by way of justification of the use of the suggested correction factors.

It need hardly be pointed out that the ordinary method of harmonic analysis makes no attempt to arrive at the most *probable* value of the harmonics from the given data, but only to determine them on the assumption that there are no harmonics present of a higher order than the number of ordinates per half period chosen for the analysis. The justification of the use of correction factors lies simply in the fact that we are not justified in making any such presumption about the higher harmonics ; and that if these *are* present, they will necessarily render the values obtained for the lower harmonics erroneous. The tables of correction factors in my paper are all founded on *reasonable assumptions* about the amplitudes of these higher harmonics ; but if it is

* Communicated by the Author.

known, in any particular case, that all the higher harmonics *are absent*, then certainly no correcting factors are required, and to apply them would be erroneous.

With p ordinates per half period, if we assume that harmonics higher than the $2p$th are absent—which is assuming the presence of harmonics up to twice the order that ordinary harmonic analysis assumes—the relations between the true Fourier constants and the obtained coefficients become

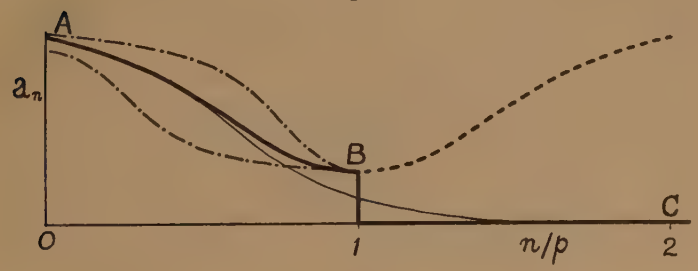
$$\mathrm{a}_n = a_n + a_{2p-n}$$

and

$$\mathrm{b}_n = b_n - b_{2p-n}$$

exactly ; which shows that the coefficient a_n needs correcting by subtracting from it the value of a_{2p-n}, and similarly for b_n.

Fig. 1.



In many cases, instead of using the tables of correction factors, the following graphical method will be sufficiently accurate ; while it is both more instructive and at the same time allows individual judgment being made to suit special cases. Let us plot the obtained coefficients a_n against n/p, and suppose that the thick line in fig. 1 represents the smooth curve through these points between $n/p=0$ and 1, continued by a line representing zero between $n/p=1$ and 2. The effect of applying correction factors is to assume that the coefficients should lie, not on the heavy broken line ABC, but on the thin line AC which reduces the ordinates to the left of $n/p=1$, and increases the (zero) ordinates an equal distance to the right by the same amount.

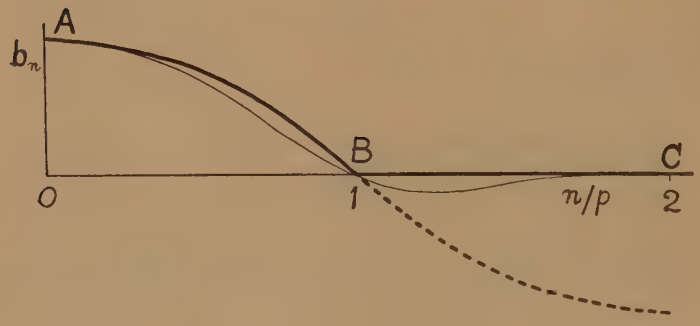
Similarly, when b_n is plotted against n/p, let the smooth curve through them be given by the thick line in AB in fig. 2. This line necessarily intersects the axis at $n/p=1$ since b_p is identically zero. The effect of the correction factors in this case is likewise to replace the thick broken line

ABC by the thin line ABC, which, at B, has half the slope of the heavy line.

The harmonics actually present in the function being analysed are obviously much more likely to follow the thin lines in figs. 1 and 2 than the heavy broken lines ; but, just as obviously, if the thick lines AB ran tangentially into the axis at or before $n/p = 1$, no corrections would be needed.

Some readers do not see how the second half of my Tables III. A and III. B * can be applied since ordinary harmonic analysis only gives harmonics up to the pth. But it is made clear, I think †, that the harmonic coefficients between the pth and the $2p$th are to be taken as given by $a_{p+n} = a_{p-n}$ and $b_{p+n} = -b_{p-n}$. The dotted lines in figs. 1 and 2 show

Fig. 2.



these coefficients as continued by these relations ; and the thin line between $n/p = 1$ and 2 may be obtained by multiplying the ordinates of the dotted curves by the correction factors in the second half of the tables, just as the thin line between $n/p = 0$ and 1 may be obtained by multiplying the ordinates of the heavy lines over this range by the correction factors in the first half of the tables.

It may happen that the points corresponding to a_n and b_n are too irregular to draw a smooth curve through them. If this is only due to a varying phase-angle, a smooth curve, of the nature of that in fig. 1, may be obtained by plotting $\sqrt{a_n^2 + b_n^2}$ against n/p. The correction factors then indicated when the corresponding thin line is drawn are then to be applied to both a_n and b_n.

* *Loc. cit.* p. 131.
† *Loc. cit.* p. 129, near bottom.

If the points on this latter curve are too irregular to draw a smooth curve through, there is nothing to give any indications about the harmonics between the pth and the $2p$th, and consequently no correction factors should be applied.

It is easily found that adopting the correction factors in the last column of Table III. B makes the tangent to the thin line in fig. 1 at $n/p=1$ cut the axis at $n/p=1+0{\cdot}15\sqrt{\pi}\equiv1{\cdot}266\ldots$ In many cases this is a very suitable slope; but in some cases, such as those in which the thick line AB in fig. 1 takes the form of either of the dot-and-dash lines, the most naturally-flowing thin line AC having, as it must have, at least 5-point contact with the thick lines at A and C, will have a slope considerably different from this at $n/p=1$. In this case it is better to take the corrections from this sketched-in line than from the tables; but use can still be made of Table III. B if desired, since all the functions in it contained an arbitrary constant to which a particular value was assigned. By the property of the functions *, if we find graphically that $n/p=1+q$ is the best intercept for the tangent to the thin line at $n/p=1$, the correction factors in Table III. B may still be used, provided that (in the case of the last column) any given value in the table is not attributed to its actual $n/p\equiv1-x$, say, but to a value of $n/p=1-qx/0{\cdot}266$. Or, in other words, the correction factor to be applied for any given value of $n/p\equiv z$, say, is the value given in the table for $n/p=1-0{\cdot}266(1-z)/q$; which is easily obtained if the function has been graphed.

There is no reason why in any work on harmonic analysis the diagrams in figs. 1 and 2 should not be attempted to be drawn, as they are exceedingly instructive and give much valuable information about the function being analysed. If it is objected that in much work only the first few harmonics are the subject of interest, and that harmonics up to $n=p$ are not of sufficient interest to justify their calculation, it may be pointed out that, when harmonics up to $n=p/2$ have been obtained, those from $p/2$ to p may be obtained by merely differencing two groups of terms that were added for the lower coefficients. After this, the diagrams, if it is possible to draw them, give a rational estimate of harmonics up to $n=2p$.

The limited accuracy of harmonic analysis must not be overlooked. Thus, suppose each ordinate was subject to a probable experimental error of ϵ, then, if the function

* *Loc. cit.* p. 128.

analysed possessed no symmetry so that it was necessary to use $2p$ ordinates spread over a whole period, it is easily found that the probable error of all the harmonic coefficients is $\epsilon/\sqrt{p}$ except in the case of the first and last cosine coefficients, $\frac{1}{2}a_0$ and $\frac{1}{2}a_n$, where it is $\epsilon/\sqrt{2p}$. The effect of this is to replace the thick lines A and B in figs. 1 and 2 by a band within which the values are uncertain.

LXXXII. *A Determination of the Stefan-Boltzmann Radiation Constant using a Callendar Radio Balance.* *By* F. E. Hoare, *A.R.C.S., B.Sc.**.

1. *Introduction.*

ACCORDING to the Stefan-Boltzmann law the rate of emission of radiation from a fully radiating surface to surroundings at the absolute zero is proportional to the fourth power of the absolute temperature of the surface.

That is

$$E' = \sigma T_1^4.$$

E' = radiation in ergs/cm.^{2}/sec.

T_1 = absolute temperature of radiator.

σ = radiation constant.

If the radiating surface is in surroundings at T_2 Abs. which are themselves full radiators, then

$$E = E' - E'' = \sigma(T_1^4 - T_2^4).$$

E'' = radiation received from surroundings.

E = net radiation of the surface.

There have been a large number of determinations of the value of σ since the law was established thermodynamically by Boltzmann†; the agreement between different observers, however, is not good.

2. *Description and Theory of Radio Balance.*

The present paper describes some experiments which were made with the Radio Balance designed by Professor Callendar‡. It is designed as an instrument to give an absolute measure of radiation, the receiver being an

* Communicated by Prof. H. L. Callendar, F.R.S.

† *Ann. der Phys.* xxii. pp. 31 and 291 (1884).

‡ Proc. Phys. Soc. xxiii. p. 1 (1910).

almost perfect "black body" so that no correction for reflexion is necessary.

In this instrument the radiation is received through a small circular aperture, caught in a copper cup 3 mm. in diameter and 8 mm. long, and is balanced or determined in absolute measure by the heat absorbed or liberated by the Peltier effect in a thermocouple through which a measured current is passed.

The Peltier couple is of iron-constantan and is soldered in the bottom of the cup, which itself is mounted in a tubular thermopile consisting of twelve couples to indicate small changes in the temperature of the cup. The lower junctions of the tubular pile are fastened to a small copper block screwed to the base of a thick hollow copper cylinder 3 cm. by 3 cm. internal measurements. The pile and cup are duplicated to compensate external disturbances, such as changes in the temperature of the surroundings. The piles and couples belonging to either cup are connected in opposition and the pile circuit is completed through a sensitive galvanometer. The deflexion of the galvanometer is proportional to the difference in temperature of the cups.

When taking a reading the radiation is allowed to be incident in one of the cups whilst the other is screened. The current through the Peltier couples is adjusted until the galvanometer, in series with the thermopiles, shows no deflexion from its zero position. The cup first exposed is then screened, the other cup exposed and at the same time the current through the couples is reversed. This should leave the balance unchanged. The method of reversal accurately eliminates the small Joule effect. If P is the value of the Peltier effect in millivolts and C is the current in milliamperes required to balance the radiation, the radiant energy received is equal to 2 PC microwatts or 20 PC ergs/sec.

In practice, owing to the impossibility of making two soldered joints exactly alike, there will be a slight deflexion of the galvanometer on changing the cup exposed to the radiation and the direction of the Peltier current, but the equivalent microwatts can be calculated if the sensitivity of the galvanometer is known in microwatts generated at the Peltier junctions to cause one scale division deflexion.

This is obtained by shielding the balance cups from radiation and reversing a known current c milliamperes through the junctions, the galvanometer deflexion D being taken. The sensitivity is given as

$$s = 2\,Pc/D \text{ microwatts per scale division,}$$

P being the Peltier coefficient in millivolts at the balance temperature.

If D′ is the steady galvanometer deflexion when radiation is incident upon cup 1 which is also being cooled by the passage of a current of C milliamperes through the Peltier junction, and D″ is the steady deflexion when cup 2 is exposed and the direction of the current reversed, then the radiation received by either cup is given by

$$2\,PC+(D'-D'')s,$$

$(D'-D'')s$ being measured in the direction of the deflexion due to passing from cup 1 to cup 2 exposed to the radiation with no current through the junctions.

The exact theory of the method of balancing the radiation and of reversal to eliminate the Joule effect is fully discussed in the paper already cited.

Assuming that the radio balance is adjusted so that its receiving aperture of area a sq. cm. is coaxial with the aperture of radius r in the water-cooled diaphragm serving to define the source, and that d is the distance in cm. between the planes of the apertures, the radiant energy E′ in ergs/sec. or microwatts, depending on the units used for σ, entering the aperture from the source at temperature T_1 Abs. is given in terms of the radiation constant by the equation

$$E' = \frac{\sigma a T_1^4 r^2}{d^2+r^2}.$$

If the source is replaced by one of equal area at a temperature T_2 Abs. the energy E″ received from the source is given by the same expression with T_2 in place of T_1.

The quantity observed is the difference

$$E=E'-E''=2\,PC+(D'-D'')s-D_0 s \text{ microwatts},$$

where D_0 is the deflexion of the galvanometer measured in the same direction as $(D'-D'')$, when first cup 1 and then cup 2 is exposed to the source at T_2 Abs.

Hence

$$\sigma = \frac{\{2\,PC+(D'-D''-D_0)s\}(d^2+r^2)}{ar^2(T_1^4-T_2^4)}$$

microwatts/cm.^{2}/degree^4.

Actually the balance has two apertures which are arranged to be equidistant on either side of the axis of the radiating aperture and the same distance from the aperture. This displacement of the centres of the receiving apertures by an amount b from the axis diminishes the radiation received in

the ratio d^2/d^2+b^2 on account of the increase of distance between the source and receiver centres and in the same ratio again because of the obliquity of the apertures. With the distances at which the measurements were made this correction is very small and is applied sufficiently accurately by the addition of the constant $2b^2$ to the factor (d^2+r^2) in the previous expression for σ.

Hence

$$\sigma = \frac{\{2\,\mathrm{PC}+(\mathrm{D}'-\mathrm{D}''-\mathrm{D}_0)s\}(d^2+r^2+2b^2)}{ar^2(\mathrm{T}_1^4-\mathrm{T}_2^4)}$$

microwatts/cm.^{2}/degree^4.

3. *Calibration of the Radio Balance.*

The Radio Balance was calibrated by finding the values of the Peltier coefficients under similar conditions to those in which it was used.

Two small heating coils were made in the following manner. A pair of copper leads were soldered to 32 cm. of S.W.G. 40 double silk-covered manganin wire at one end and an exactly similar pair at the other, so that the potential and current leads joined the manganin wire at the same place. S.W.G. 38 double silk-covered copper wire was used for the leads to keep the conduction losses small. One pair of leads was then pulled through a glass capillary tube of about 2·5 mm. external diameter and 3 cm. long, so that the soldered join to the manganin wire was just inside the tube and thus insulated by it. The manganin wire was then wound back on the glass tube to a distance of about 6 mm. from the end. By having a double layer of wire all the 32 cm. of wire was wound on this length. The remaining soldered joint was insulated and the coil held together by a coat of shellac dissolved in absolute alcohol, which was allowed to become thoroughly dry before the coil was used. The other coil was made in a similar manner, and the resistance was made to agree to less than 1 part in 1000 with that of the first coil by careful adjustment and testing with a potentiometer. The resistance of each coil was approximately 9 ohms; when complete and the shellac thoroughly dry they fitted tightly into the cups of the Radio Balance, the top of the coil being at least 2 mm. below the top of the cup. The coils were put one in each cup of the Radio Balance and a little vacuum oil was put in to make a better thermal connexion between the coils and the walls of the cups. This is very necessary, for if there is a large resistance to the flow of heat from the coil to the cup

the values obtained for the Peltier coefficients will be too large.

The current was made to flow through one of the coils and one pair of leads connected to the other coil. In this manner, by having the same current through the leads of each coil, the heating effects in the leads are accurately compensated.

The method of taking observations was to balance the heating effect in one coil against the cooling effect of the Peltier couple in one cup and the heating effect in the other. The current was then sent through the second coil and one pair of the leads to the first coil, and the current in the Peltier circuit reversed simultaneously. Knowing the current in the coil circuit and the potential across the coil the microwatts expended in the coil can be deduced.

If

W = microwatts expended in coil,

$(D'-D'')s$ = scale microwatts,

C = current in Peltier circuit in milliamperes,

the value of P is given by

$$P = \frac{W-(D'-D'')s}{2C} \text{ millivolts.}$$

This is the value of P at the temperature of the Radio Balance.

The currents in the coil circuit and the Peltier circuit were found by measuring the potentials across known standard resistances of approximately one ohm each, which had been carefully compared with N.P.L. standards.

The potentiometer used for potential measurements in all these experiments was the direct reading type 0–90 millivolts as made by the Cambridge Inst. Co. The scale, which read to one microvolt, was adjusted by means of a Weston standard cell which had been compared with N.P.L. standards. This cell was a hermetically sealed H type and the E.M.F. was taken as

1·0183 volts at 20° C.

with a temperature correction given by

$$V_t = V_{20} - 0{\cdot}0000406\,(t-20),$$

where t is the temperature of the cell in degrees centigrade.

The temperature of the Radio Balance was measured with a specially constructed mercury thermometer which fitted right into the body of the instrument. The thermometer was graduated in half-degrees centigrade and no difficulty was experienced in estimating to a tenth of a degree. The

temperature was varied by varying the temperature of the room, closing all the windows and doors and turning the heating apparatus full on for the higher temperatures, and leaving the windows and doors open, but carefully screening the Radio Balance from draughts, for the lower temperatures.

The values found for the Peltier coefficients were as follows :—

Temp. °C. ...	15°	17°	19°	21°	23°	25°
P millivolts...	14·85	14·98	15·11	15·25	15·38	15·51

These results are represented by the equation

$$P_t = P_{20} + 0{\cdot}066\,(t-20).$$

In the series of values obtained for P the deviation from a straight line when P was plotted against t was always less than 1 in 1000.

4. *Arrangement of Apparatus.*

The source of radiation used in these experiments was a wire-wound electric furnace, the temperature of which was measured with a platinum resistance thermometer.

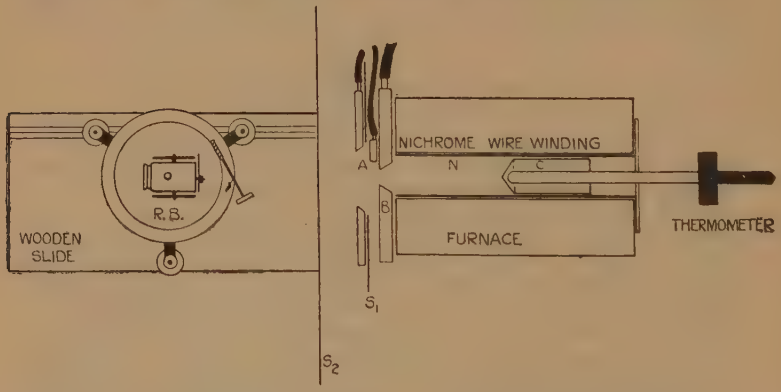
A heating solenoid of nichrome wire was wound on a quartz cylinder of about one and three-quarter inches internal diameter, the wire being wound closer at the ends than in the middle in order to compensate for the heat losses from the ends of the tube. This tube was surrounded with other concentric tubes and wrappings of insulating material. Into the quartz tube fitted fairly closely a nickel cylinder a sixteenth of an inch thick. This cylinder extended the whole length of the tube and no part of it was visible when taking readings. A nickel block with one end turned up to a blunt cone loosely fitted into this tube, so that the cone end was approximately in the centre of the furnace. The cone end of the nickel block formed the radiating surface and was made this shape to prevent direct reflexion into the Radio Balance. The other end of the nickel block was bored to take a platinum resistance thermometer, the coil being completely enclosed in the block and near the radiating surface. On the end of the furnace was fitted a water-cooled diaphragm made of brass and blackened, the water space between the back and front being half an inch. The aperture in the diaphragm could be closed with a water-cooled shutter mounted directly in front of the diaphragm. The diameter of the diaphragm was a little greater than that of the end of the furnace in order that no radiation from the heated parts

of the furnace could affect the Radio Balance. It is important that the flat side of the water-cooled diaphragm should be towards the receiver and the bevelled side towards the furnace to prevent any possible reflexion of heat by the bevel into the receiver. The receiving apertures of the Radio Balance were similarly bevelled with the flat side towards the source.

5. *Measurements.*

The diameters of the apertures in front of the cups were measured with a Hilger measuring microscope reading to 0·0001 cm.

Figure showing General Arrangement of Furnace and Radio Balance.



A. Movable Water-Cooled Shutter.
B. Water-Cooled Diaphragm.
C. Nickel Block.
N. Nickel Cylinder.
S_1S_2. Screens.
R.B. Radio Balance.

The mean of 52 measurements for the diameter of aperture 1 gave 0·2099 cm. diameter or 0·03464 sq. cm. area.

For aperture 2 the mean of 50 measurements gave 0·2083 cm. diameter or 0·03411 sq. cm. area.

The mean area was taken as $a = 0{\cdot}03411$ sq. cm.

The value of b was obtained by measuring with the same microscope the shortest distance between the apertures and adding the mean diameter of the apertures to this distance.

The value found was $b = 0{\cdot}579$ cm.

The diameter of the aperture in the diaphragm was measured, whilst water was flowing through it, with a Cambridge Inst. Co. travelling microscope reading to 0·0001 cm.

The value found as a mean of 38 measurements was $2r = 2{\cdot}0527$ cm.

The distance between the source and the receiver, which is the distance between the opposing flat surfaces, was measured with a micrometer distance piece reading to 0·0001 cm.

The current in the Peltier circuit was measured by taking the potential across a standard resistance as previously described.

The platinum thermometer used for measuring the temperature of the furnace was of the usual type as made by the Cambridge Inst. Co., having a fundamental interval of approximately one ohm.

The thermometer was used in conjunction with a Callendar Griffiths' bridge and a sensitive coil galvanometer The bridge was calibrated by the usual substitution method and the small corrections found were applied to the coils. After the experiments had been proceeding for some time the coils were again calibrated. This calibration agreed with the previous one to the accuracy obtainable by this method.

The fundamental interval of the thermometer was determined about once a week during the course of the experiments and showed a slight change of 0·0003 ohm over this period. The ice point changed by 0·0005 ohm in the same period.

The temperature was calculated from the equation

$$pt = \frac{R - R_0}{R_{100} - R_0} \times 100,$$

and corrected to the gas scale by the equation

$$t - pt = d(t - 100)t.$$

pt = temperature on platinum scale.

t = temperature on centigrade scale.

$d = 1{\cdot}5 \times 10^{-4}$.

When taking a reading the Callendar Griffiths' bridge was set to correspond with a previously decided temperature and the bridge galvanometer spot kept within limits corresponding to a fifth of a degree centigrade on either side of the balance position by hand manipulation of four rheostats in series with the furnace and the 110 volt mains.

The temperature of the water circulating in the diaphragm was measured to a tenth of a degree centigrade on inflow and outflow with mercury thermometers totally immersed in the stream. The mean of these temperatures was taken as T_2. The difference between the two thermometers rarely exceeded 0·5° C.

6. *Method of taking Observations.*

The Radio Balance was placed on a long wooden slide with a groove to take the feet of the instrument, in order that it could be moved along the axis through the centre of the radiating aperture. The slide and the Radio Balance were carefully levelled and centred, using a spirit level and steel rules. At no point was the centre of the Radio Balance more than 2 mm. off the horizontal axis through the centre of the radiating aperture; and the error introduced by this is much less than 1 part in 1000 for the distances used.

To prevent extraneous radiation from reaching the Radio Balance two screens were placed between the source and the receiver. The one nearer the furnace was water-cooled, having a central aperture of 10 cm. and was 5 cm. from the furnace. The other was of tin plate with a 4 cm. aperture situated 15 cm. from the furnace. Both screens were blackened on the side towards the receiver, and the apertures were arranged to be coaxial with the radiating aperture.

The Radio Balance apertures were exposed or screened by moving a shutter in close contact with the plane of the apertures and a screen on the front of the instrument. Both the shutter and the movable screen were blackened on the side remote from the furnace and gilded on the other.

The Radio Balance having been set with the plane of its apertures at a known distance from and parallel to the plane of the aperture in the water-cooled diaphragm, the latter was covered with the water-cooled shutter. First one cup of the receiver and then the other were exposed to the radiation from the shutter and surrounding bodies at a temperature T_2. The small galvanometer deflexion on changing from one cup to the other was noted. This is D_0 in the expression given previously for σ. The shutter was then removed and one cup of the Radio Balance exposed to the radiation from the nickel block, the current through the Peltier junctions being adjusted so that the difference in temperature of the cups was very small. Galvanometer readings were taken every minute for five successive minutes, the potential across the standard resistance being taken at the same time. The second cup was then exposed to the radiation, the Peltier current reversed and a similar series of readings taken. The mean of each series was used in calculating the value of σ.

The temperature of the Radio Balance and the inflow and outflow temperatures of the water were taken before and after each set of readings, and found to be very constant.

7. *Results.*

Mean area of Radio Balance apertures... 0·03437 sq. cm.
Diameter of water-cooled aperture ..... 2·0527 cm.
Displacement of balance aperture centres from axis. 0·579 cm.

The following table gives the value of $\sigma \times 10^5$ in ergs/sec./cm.^{2}/degree^4 :—

Date 1928.	Temp. furnace.	Temp. water.	Temp. Radio Balance.	Total micro-watts.	Dist. of furnace.	Value of $\sigma \times 10^5$.
April 26 ...	786·00° C.	16·5° C.	21·3° C.	200·15	36·041 cm.	5·751
,, ...	,,	,,	21·3	200·37	,,	5·758
,, ...	777·20	,,	21·0	261·74	31·010	5·758
,, ...	,,	,,	21·1	260·73	,,	5·735
,, ...	,,	,,	21·1	371·10	26·029	5·756
,, ...	,,	,,	21·1	370·53	,,	5·747
April 27 ...	716·55	16·9	19·7	291·69	26·033	5·749
,, ...	,,	,,	19·7	291·57	,,	5·747
,, ...	,,	,,	19·7	203·88	31·071	5·720
,, ...	,,	,,	19·6	204·27	,,	5·731
,, ...	,,	,,	19·3	151·85	36·053	5·733
,, ...	,,	,,	19·2	152·10	,,	5·742
June 8 ...	772·27	19·3	22·0	541·70	21·195	5·681
,, ...	,,	,,	21·6	361·02	26·072	5·723
,, ...	,,	,,	21·6	359·23	,,	5·694
,, ...	,,	,,	21·5	257·04	31·008	5·760
,, ...	,,	,,	21·5	256·02	,,	5·737
June 9 ...	831·85	19·4	20·5	318·90	30·992	5·730
,, ...	,,	,,	20·5	320·14	,,	5·752
,, ...	,,	,,	20·6	452·03	26·070	5·736
,, ...	,,	,,	20·6	451·71	,,	5·732
,, ...	,,	,,	20·6	237·00	35·985	5·725
,, ...	,,	,,	20·6	237·18	,,	5·729
June 10 ...	985·51	19·6	20·0	400·76	35·963	5·734
,, ...	,,	,,	20·0	400·50	,,	5·727
,, ...	,,	,,	20·0	536·35	31·159	5·763
,, ...	,,	,,	20·0	535·76	,,	5·756
,, ...	,,	,,	20·0	763·51	26·072	5·747
,, ...	,,	,,	19·6	1154·5	21·089	5·692
,, ...	,,	,,	19·7	1156·7	,,	5·703
June 11 ...	821·47	19·1	19·6	307·05	31·077	5·744
,, ...	,,	,,	19·9	304·39	,,	5·694
,, ...	,,	,,	19·4	227·96	35·975	5·713
,, ...	,,	,,	19·2	229·90	,,	5·762
,, ...	,,	,,	19·0	176·23	41·085	5·758
,, ...	,,	,,	19·1	175·73	,,	5·741
,, ...	,,	,,	19·2	431·41	26·195	5·738
,, ...	,,	,,	19·4	431·28	,,	5·736

Mean value of $\sigma = 5{\cdot}735 \times 10^{-5}$ erg/sec./cm.^{2}/degree^4.

8. *Discussion of Methods.*

The condition which is theoretically necessary in a determination of the radiation constant is that both the source and the receiver should be full radiators or "black bodies."

In the foregoing experiments this condition has been realized as far as is possible in experimental work of this description, by having constant temperature enclosures with good radiating walls and apertures small in comparison with the dimensions of the enclosure.

Keene * has been the only other observer using a similar method to determine the radiation constant who has endeavoured to obtain "black body" conditions in radiator and receiver. In his paper he states that owing to the water-cooled diaphragm on the furnace being in the reverse direction to that used above, his mean value of $5{\cdot}89 \times 10^{-5}$ c.g.s. units may be as much as 2 per cent. high, through heat reflected from the bevel re-entering the receiver. A range of only 23° C. (1097°–1120°) was used, and the distance between the source and receiver was only varied by 0·023 cm. The receiver was an aniline Thermoscope of rather high thermal capacity which was calibrated by an electrical method.

Coblentz † has made a determination of this constant using a modified Ångström Pyrheliometer. His value $5{\cdot}722 \times 10^{-5}$ c.g.s. units, is the mean of a large number of results using different receivers, but all of similar construction. The variation in the values of σ is about 4 per cent., after a correction for reflexion, separately determined, has been applied to the observed values.

Other experimenters using different methods, such as the ratio of emissivities, have obtained a value for σ of the order of $5{\cdot}7 \times 10^{-5}$ c.g.s. units. These results have not been discussed in detail here as the principles of the methods used differ from those of the methods already mentioned.

Lewis and Adams ‡ have used the theory of ultimate rational units in order to calculate the value of σ. Using data based upon the electronic charge e, the gas constant R and the Faraday equivalent F, they obtain the value $5{\cdot}7 \times 10^{-5}$ c.g.s. units for the radiation constant.

More recently Millikan § using Planck's equation for the distribution of energy in the spectrum of a "black body,"

* Proc. Roy. Soc. lxxxviii. p. 49 (1913).
† Bull. Bur. Stds. xii. p. 503 (1916).
‡ Phys. Rev. (2) iii. p. 92 (1914).
§ Phil. Mag. xxxiv. p. 1 (1916).

has calculated the value of σ. The value he obtains is $5{\cdot}72 \pm {\cdot}034 \times 10^{-5}$ c.g.s. units.

From a critical examination of the values of σ obtained by a variety of methods, it now seems well established that the value of this constant lies in the range $5{\cdot}70$ to $5{\cdot}75 \times 10^{-5}$ c.g.s. units.

9. *Conclusion.*

The concordance of the results obtained with the Radio Balance under widely differing conditions shows that the method used for evaluating the absolute measure of radiation is extremely satisfactory, and that the instrument is well suited for this purpose. It has the further advantages of being easy to manipulate, quickness in working, and accuracy in the necessary measurements.

I wish to express my gratitude to Professor Callendar for the continual advice he has given me, and the kindly interest he has shown throughout the course of the experiments.

LXXXIII. *Note on a Type of Determinantal Equation.* By R. C. J. Howland, *M.A., M.Sc., University College, London* *.

EQUATIONS of the type

$$\begin{vmatrix} a_{11}-\lambda, & a_{12}, & \ldots\ldots, & a_{1n} \\ a_{21}, & a_{22}-\lambda, & \ldots\ldots, & a_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ a_{n1}, & a_{n2}, & \ldots\ldots, & a_{nn}-\lambda \end{vmatrix} = 0 \quad . \quad (1)$$

occur frequently in vibration and other problems, and in many such problems not more than two, the highest, values of λ are of interest.

When equation (1) is expanded, the coefficient of $(-\lambda)^n$ is unity; that of $(-\lambda)^{n-1}$ is the sum of the diagonal elements; while that of $(-\lambda)^{n-2}$ is the sum of $n(n-1)/2$ determinants of the second order, and is readily calculated. The remaining coefficients, however, appear as the sums of determinants of the third or higher orders. Experience shows that the calculation of such determinants, using a

* Communicated by the Author.

calculating machine, is not only laborious, but is of a type in which it is easy to fall into error.

It is the object of the present note to show that the equation may also be solved by an application of the root-squaring method *. The calculations involved are about as extensive as those needed for the direct solution, but they are of a kind better adapted to the calculating machine, and for this reason the method may prove to have some advantage in practice.

In order to form an equation whose roots are the squares of those of (1), we first form a new equation from (1) by changing the sign of λ and then multiply the two determinants in matrix fashion, rows by columns. This gives the new equation in the form

$$\begin{vmatrix} A_{11}-\lambda, & A_{12}, & \ldots, & A_{1n} \\ A_{21}, & A_{22}-\lambda, & \ldots, & A_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ A_{n1}, & A_{n2}, & \ldots, & A_{nn}-\lambda \end{vmatrix} = 0 \quad \ldots \quad (2)$$

where $$A_{rs} = \sum_{t=1}^{n} a_{rt} a_{ts}.$$

Since A_{rs} consists of a sum of simple products, its calculation is of a type to which a calculating machine is well adapted.

The process is now repeated with equation (2), and continued until the roots are so far separated that the first two can be estimated from three terms only of the equation; these, as we have seen, are readily calculated.

Consider, for example, the equation

$$\begin{vmatrix} 25-\lambda, & 38, & 39, & 31, & 17 \\ 38, & 64-\lambda, & 69, & 56, & 31 \\ 39, & 69, & 81-\lambda, & 69, & 39 \\ 31, & 56, & 69, & 64-\lambda, & 38 \\ 17, & 31, & 39, & 38, & 25-\lambda \end{vmatrix} = 0. \quad \ldots \quad (3)$$

which occurred in a problem of the whirling of a shaft.

* Whittaker & Robinson, 'The Calculus of Observations,' pp. 106 *et seq.* (London, 1924).

The first two roots of this equation were found to be 239·5 and 14·55. The first three terms of the expanded equation are

$$\lambda^5-259\lambda^4+4705\lambda^3 \ldots\ldots\ldots=0. \quad . \quad . \quad . \quad (4)$$

If the highest root is estimated from the coefficient of λ^4 only, we obtain $\lambda_1=259$. If the second root is estimated from the ratio of the coefficients of λ^3 and λ^4, the result is 18·2.

A first application of the root-squaring process to (3) gives

$$\begin{vmatrix} 4840-\lambda^2, & 8336, & 9558, & 8224, & 4727 \\ 8336, & 14398-\lambda^2, & 16560, & 14285, & 8224 \\ 9558, & 16560, & 19125-\lambda^2, & 16560, & 9558 \\ 8224, & 14285, & 16560, & 14398-\lambda^2, & 8336 \\ 4727, & 8224, & 9558, & 8336, & 4840-\lambda^2 \end{vmatrix} =0$$

The first three terms of this equation are

$$\lambda^{10}-57601\lambda^8+1{\cdot}350\times10^7\lambda^6 \ldots.=0. \quad . \quad . \quad (5)$$

From the coefficient of λ^8 we now estimate the first root as

$$\lambda_1=\sqrt{57601}=240,$$

while the ratio of the coefficients of λ^6 and λ^8 leads to

$$\lambda_2=\sqrt{1350/5{\cdot}76}=15{\cdot}3.$$

The approximation is already quite good.

In repeating the process, it is necessary to work to seven or eight figures if the coefficients are to be accurate to three or four. The resulting determinant is therefore rather long and will not be written down. It leads to the equation

$$\lambda^{20}-3{\cdot}291\times10^9\lambda^{16}+1{\cdot}569\times10^{14}\lambda^{12}-\ldots=0 \quad . \quad . \quad (6)$$

From this we have

$$\lambda_1=(3{\cdot}291\times10^9)^{\frac{1}{4}}=239{\cdot}5,$$

$$\lambda_2=(1{\cdot}569\times10^5/3{\cdot}291)^{\frac{1}{4}}=14{\cdot}78.$$

The error in λ_2 is about 1·6 per cent., and, since the frequency depends on $\sqrt{\lambda}$, the error in this will be less than 1 per cent. Thus the first two roots are obtained with sufficient accuracy for most practical purposes.

In practice it is necessary to judge the degree of approximation that has been reached by watching the

convergence of the sequence of estimates given by the successive equations such as (4), (5), and (6). The three successive estimates of λ_2, namely 18·2, 15·3, 14·78, indicate a rapid convergence to a value not very different from the last of them. Such an indication can usually be accepted with confidence, since it is generally known that the roots of the initial equation are real and well separated, conditions which are known to be sufficient to make the process a rapidly convergent one.

LXXXIV. *Heaviside's Formulæ for Alternating Currents in Cylindrical Wires.* *By* T. J. I'A. Bromwich *.

IT was certainly due to Heaviside † that two correlated problems of this type were fully solved in terms of Bessel-functions; but of late years text-books have usually given the much less convenient solutions, obtained later ‡ by Lord Kelvin in terms of the *ber* and *bei* functions. Lord Kelvin himself had certain numerical results tabulated from his formulæ, being (apparently) unaware that equivalent values had been previously tabulated by Heaviside: in other respects Lord Kelvin was fully aware of the importance of Heaviside's work. It is, in fact, due to Heaviside's work that we obtain the (now commonplace) view that the seat of the electromagnetic energy is the surrounding medium: that this energy gradually soaks into the conducting wire, and is there used up in heating the wire.

Hitherto (so far as I know) no proofs have been given of Heaviside's formulæ given in § 2 below; thus, although the results are some 40 years old, it may be of service to provide proofs, and at the same time to direct attention to the advantages obtained by using these formulæ.

§ 1. *Preliminary Formulæ.*

In Heaviside's discussion of an alternating current flowing along a cylindrical wire, the fundamental equations are (writing p for $\partial/\partial t$):

$$\frac{4\pi}{\sigma}\mathrm{E}_1=-\frac{\partial \mathrm{H}_2}{\partial z},\quad \frac{4\pi}{\sigma}\mathrm{E}_3=\frac{1}{r}\frac{\partial (r\mathrm{H}_2)}{\partial r},\quad -\mu p\mathrm{H}_2=\frac{\partial \mathrm{E}_1}{\partial z}-\frac{\partial \mathrm{E}_3}{\partial r},$$

* Communicated by the Author.

† Papers, vol. i. p. 362; and vol. ii. p. 97.

‡ Lord Kelvin himself refers repeatedly to the work done by Heaviside in this connexion.

where $(E_1, 0, E_3)$ and $(0, H_2, 0)$ denote the electric and magnetic forces (in cylindrical coordinates r, θ, z), and σ, μ are the specific resistance and permeability of the wire. In most practical applications the fields are independent of z and the familiar methods of solution give

$$E_1 = 0, \qquad E_3 = A I_0(qr), \qquad H_2 = \frac{4\pi}{\sigma q} A I_1(qr),$$

where $$q^2 = 4\pi\mu p/\sigma.$$

Without going further into the general theory of such operational symbols *, we may pass at once to the case of alternating currents, for which (assuming a time-factor e^{int}) we can write simply

$$p = in.$$

Then $$q^2 = 4\pi in\mu/\sigma = (4\pi n\mu/\sigma) e^{i\pi/2},$$

and so $$qr = r\sqrt{4\pi n\mu/\sigma}\, e^{i\pi/4}.$$

The total current in the wire is

$$C = \int_0^a \frac{2\pi}{\sigma} E_3 r\, dr = \tfrac{1}{2} a H_2(a) = \frac{2\pi A a}{\sigma q} I_1(qa),$$

and the effective resistance is accordingly given by

$$\frac{E_3(a)}{C} = \left(\frac{\sigma}{\pi a^2}\right) \frac{qa I_0(qa)}{2 I_1(qa)}.$$

When $p = 0$ this expression reduces to $\sigma/\pi a^2 = R$, the steady current-resistance; but in general it is an operator, and is called by Heaviside the *resistance-operator*.

§ 2. *Certain Series derived from Bessel Functions.*

Let us write $$qr = x e^{i\pi/4},$$

where x is real, and put $I_0(qr) = u$;

also let v denote the complex number conjugate to u.

It will be convenient to write further

$$\xi = \log x, \quad x = e^{\xi},$$

so that

$$\frac{d}{d\xi} = x\frac{d}{dx} \quad \text{and} \quad \frac{d^2u}{d\xi^2} = x\frac{d}{dx}\left(x\frac{du}{dx}\right) = r\frac{d}{dr}\left(r\frac{du}{dr}\right)$$

* For a convenient introduction (with references to Heaviside's work and to earlier papers of my own) the reader may consult Dr. H. Jeffreys's Tract (No. 23 of the Cambridge Mathematical and Physical Tracts, 1927).

Now the differential equation for $I_0(gr)$ gives

$$r\frac{d}{dr}\left(r\frac{du}{dr}\right)=q^2r^2u=\iota x^2u=\iota e^{2\xi}u,$$

and so the final equation for u in terms of ξ is

$$\frac{d^2u}{d\xi^2}=\iota e^{2\xi}u. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since ξ is real, we can obtain the equation for v by changing the sign of ι in (1), and then we have

$$\frac{d^2v}{d\xi^2}=-\iota e^{2\xi}v. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Consider now the actual formula for u: from the familiar series for $I_0(gr)$ we see that

$$u=1+\frac{\iota x^2}{2^2}-\frac{x^4}{2^2.4^2}-\frac{\iota x^6}{2^2.4^2.6^2}+\frac{x^8}{2^2.4^2.6^2.8^2}+\ldots,$$

from which it is evident that the formulæ are simplified by writing *

$$x^2=4z, \quad \log z=\zeta, \quad \text{so that} \quad 2\xi=\zeta+\log 4 \quad . \quad (3)$$

Then we have

$$u=1+\frac{\iota z}{1^2}-\frac{z^2}{1^2.2^2}-\frac{\iota z^3}{1^2.2^2.3^2}+\frac{z^4}{1^2.2^2.3^2.4^2}+\ldots, \quad (4)$$

and the equations (1) and (2) reduce to the forms

$$u''=\iota e^{\zeta}u, \qquad v''=-\iota e^{\zeta}v, \quad . \quad . \quad . \quad . \quad (5)$$

where accents denote differentiation with respect to ζ.

Multiply equations (5) by u, v and *add*: then we have

$$uv''+u''v=0,$$

which may be written

$$\frac{d^2}{d\zeta^2}(uv)=2u'v'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Differentiate (6) again and the result will be

$$\frac{d^3}{d\zeta^3}(uv)=2(u''v'+u'v'')=2\iota e^{\zeta}(uv'-u'v). \quad . \quad . \quad (7)$$

The function on the right-hand side of (7) is of importance

* This z is the same as Heaviside's (Electrical Papers, vol. ii. p. 91). Also $u=M+\iota N$, $v=M-\iota N$ in his notation.

in the future work ; and to obtain a convenient notation, it may be noted that from (4) we have

$$u=1+\iota e^{\zeta}+O(e^{2\zeta}), \qquad v=1-\iota e^{\zeta}+O(e^{2\zeta}),$$
$$u'=\iota e^{\zeta}+O(e^{2\zeta}), \qquad v'=-\iota e^{\zeta}+O(e^{2\zeta}).$$

Thus $$uv'-u'v=-2\iota e^{\zeta}+O(e^{2\zeta}).$$

It is therefore convenient to use the real function w defined by

$$2w=\iota(uv'-u'v), \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that *the first term in w is* e^{ζ}.

It will now be seen that (7) reduces to

$$\frac{d^2}{d\zeta^2}(uv)=4e^{\zeta}w. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Also $$\frac{dw}{d\zeta}=\tfrac{1}{2}\iota(uv''-u''v)=e^{\zeta}(uv). \quad . \quad . \quad . \quad (10)$$

Remembering the form of (4) we see that

$$uv=1+\tfrac{1}{2}e^{2\zeta}+O(e^{4\zeta}).$$

Thus we can assume that

$$\left.\begin{aligned} uv&=1+A_1e^{2\zeta}+A_2e^{4\zeta}+A_3e^{6\zeta}+\ldots \\ w&=e^{\zeta}(1+B_1e^{2\zeta}+B_2e^{4\zeta}+B_3e^{6\zeta}+\ldots) \end{aligned}\right\}, \quad . \quad . \quad (11)$$

and so, substituting in (9) and (10), the coefficients A_n, B_n are given by

$$\left.\begin{aligned} &2^3A_1=4, \quad 4^3A_2=4B_1, \quad 6^3A_3=4B_2, \ \ldots \\ \text{and} \quad &3B_1=A_1, \quad 5B_2=A_2, \quad 7B_3=A_3, \ \ldots \end{aligned}\right\}. \quad . \quad (12)$$

From (12) it is easy to see that

$$\left.\begin{aligned} &A_1=\frac{1}{2}, \ \frac{A_2}{A_1}=\frac{1}{2^3}\cdot\frac{1}{6}, \ \frac{A_3}{A_2}=\frac{1}{3^3}\cdot\frac{1}{10}, \ \frac{A_4}{A_3}=\frac{1}{4^3}\cdot\frac{1}{14}, \ldots \\ \text{and} \\ &B_1=\frac{1}{6}, \ \frac{B_2}{B_1}=\frac{1}{2^3}\cdot\frac{1}{10}, \ \frac{B_3}{B_2}=\frac{1}{3^3}\cdot\frac{1}{14}, \ \frac{B_4}{B_3}=\frac{1}{4^3}\cdot\frac{1}{18}, \ldots \end{aligned}\right\}. \quad (13)$$

Thus, from (11) and (13), we find the first pair of fundamental series

$$uv=P_1=1+\frac{z^2}{2}\left(1+\frac{z^2}{2^3.6}\left(1+\frac{z^2}{3^3.10}\left(1+\frac{z^2}{4^3.14}\left(1+\ldots. \quad (14)\right.\right.\right.$$

$$\left.\begin{aligned} &\text{and} \qquad w=\frac{\iota}{2}(uv'-u'v)=zP_2, \\ &\text{where} \\ &P_2=1+\frac{z^2}{6}\left(1+\frac{z^2}{2^3.10}\left(1+\frac{z^2}{3^3.14}\left(1+\frac{z^2}{4^3.18}\left(1+\ldots\right.\right.\right.\right. \end{aligned}\right\}. \quad (15)$$

It is useful to note the numerical values of these successive denominators, which are in (14):

2, 48, 270, 896, ...

and in (15): 6, 80, 378, 1152, ...

The next series which it is useful to obtain is

$$u'v'=\frac{1}{2}\frac{d^2}{d\zeta^2}(uv)=\frac{1}{2}\frac{d^2P_1}{d\zeta^2}, \text{ from (6).}$$

On differentiating (14) this gives

$$\left.\begin{aligned} &u'v'=z^2P_3, \\ &\text{where} \\ &P_3=1+\frac{z^2}{2.6}\left(1+\frac{z^2}{2^2.3.10}\left(1+\frac{z^2}{3^2.4.14}\left(1+\ldots\right)\right)\right. \end{aligned}\right\}. \quad (16)$$

Here the denominators are found to be

12, 120, 504, 1440, ...

Finally we shall use also

$$uv'+u'v=\frac{d}{d\zeta}(uv)=\frac{dP_1}{d\zeta},$$

and from (14) this gives

$$\left.\begin{aligned} &uv'+u'v=z^2P_4, \\ &\text{where} \\ &P_4=1+\frac{z^2}{2^2.6}\left(1+\frac{z^2}{2.3^2.10}\left(1+\frac{z^2}{3.4^2.14}\left(1+\ldots\right)\right)\right. \end{aligned}\right\}. \quad (17)$$

The sequence of denominators is here

24, 180, 672, 1800, ...

It may be convenient to note that corresponding terms in these four series are arranged in order of numerical magnitude, so that

$$P_1>P_2>P_3>P_4.$$

It may also be of interest to observe that the four series are connected by the simple identity

$$P_1P_3-P_2^2=\tfrac{1}{4}z^2P_4^2, \text{ so that } P_1P_3>P_2^2. \quad (18)$$

In fact we have

$$\frac{1}{4}(uv'+u'v)^2-\frac{1}{4}(uv'-u'v)^2=(uv)(u'v'),$$

or

$$\frac{1}{4}(z^2\mathrm{P}_4)^2+(z\mathrm{P}_2)^2=\mathrm{P}_1(z^2\mathrm{P}_3),$$

and, on division by z^2, this reduces to (18).

As a direct verification, we find that (up to z^4)

$$\mathrm{P}_1\mathrm{P}_3=1+\left(\frac{1}{2}+\frac{1}{12}\right)z^2+\left(\frac{1}{96}+\frac{1}{24}+\frac{1}{1440}\right)z^4+\ldots$$

$$=1+\frac{7}{12}z^2+\frac{19}{360}z^4+\ldots,$$

$$\mathrm{P}_2{}^2=1+\frac{1}{3}z^2+\left(\frac{1}{36}+\frac{1}{240}\right)z^4+\ldots$$

$$=1+\frac{1}{3}z^2+\frac{23}{720}z^4+\ldots.$$

Thus, on subtracting, we see that

$$\mathrm{P}_1\mathrm{P}_3-\mathrm{P}_2{}^2=\frac{1}{4}z^2+\frac{1}{48}z^4+\ldots$$

$$=\frac{1}{4}z^2\left(1+\frac{1}{12}z^2+\ldots\right),$$

while $$\mathrm{P}_4{}^2=1+\frac{1}{12}z^2+\ldots,$$

so that the general formula (18) is verified as far as terms in z^4.

For comparison with Heaviside's work it is convenient to observe that he writes

$$\mathrm{M}+\iota\mathrm{N},\ \mathrm{M}-\iota\mathrm{N}$$

for u, v respectively.

Thus in the notation used above, we find that,

$$\left.\begin{aligned}\mathrm{P}_1&=\mathrm{M}^2+\mathrm{N}^2\\ z\mathrm{P}_2&=\tfrac{1}{2}r(\mathrm{MN}'-\mathrm{M}'\mathrm{N})\\ z^2\mathrm{P}_3&=\tfrac{1}{4}r^2(\mathrm{M}'^2+\mathrm{N}'^2)\\ z^2\mathrm{P}_4&=r(\mathrm{MM}'+\mathrm{NN}')\end{aligned}\right\},\quad\ldots\quad(19)$$

where, in (19), *as in Heaviside's formulæ, the accents refer to differentiations of* M, N *with respect to* r.

Actually the functions M, N are identical with those for which Lord Kelvin introduced (at a later date) the notation *ber*, *bei*; but neither he nor any others (of those who have worked at the subject in ignorance of Heaviside's formulæ) gave the formulæ (18) and (19).

§ 3. *Applications to longitudinal alternating currents.*

In Heaviside's operational method we write

$$q^2=4\pi\mu p/\sigma, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where, as above, $p=d/dt$, and σ, μ are the specific resistance and the permeability. Thus *if we write* R *for the steady-current resistance per unit length of the wire*, we have

$$\mathrm{R}=\sigma/\pi a^2,$$

and

$$q^2a^2=4\mu p/\mathrm{R}.$$

In the case of alternations of frequency $n/2\pi$, we can write effectively $p=\iota n$, taking q then as a complex with a positive real part.

Thus

$$q^2a^2=4\mu\iota n/\mathrm{R},$$

or

$$qa=\sqrt{\frac{4\mu n}{\mathrm{R}}}\,e^{\iota\pi/4}.$$

That is, in the notation of § 2,

$$x=2\sqrt{\mu n/\mathrm{R}},$$

or *

$$z=\mu n/\mathrm{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Heaviside has shown that the resistance-operator of the wire (per unit length) is given by the formula (see § 1)

$$\tfrac{1}{2}\mathrm{R}qa\,\mathrm{I}_0(qa)/\mathrm{I}_1(qa), \quad . \quad . \quad . \quad . \quad . \quad (22)$$

which reduces to R, as it should, when the current is *steady*, so that we can write $p=0$ or $q=0$.

It is usual for numerical work to express the resistance-operator in the form

$$\mathrm{R}'+\mathrm{L}'p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and then to call R', L' *the high-frequency resistance and self-inductance*, per unit length of the wire.

Using the notation of (4), (5), we find from (22) and (23),

$$\mathrm{R}'+\mathrm{L}'p=\mathrm{R}\left(\frac{qa}{2}\right)^2\frac{u}{u'}=\mathrm{R}\frac{\iota z}{2}\frac{1}{u'v'}\{(uv'+u'v)+(uv'-u'v)\}.$$

* In vol. i. of his Papers, Heaviside uses the alternative notation,

$$y=(4z)^2,$$

but this seems less convenient in most applications.

On substituting from (15)–(17) we see that

$$\frac{R'}{R}=\frac{P_2}{P_3} \quad \text{and} \quad \frac{L'n}{R}=\frac{\frac{1}{2}zP_4}{P_3}, \quad . \quad . \quad . \quad (24)$$

the two formulæ given by Heaviside*.

For example, let $z=10$ or $\mu n=10R$.

Then $P_2=44{\cdot}507$, $P_3=17{\cdot}755$, $P_4=7{\cdot}8454$,

and so $\frac{R'}{R}=\frac{44{\cdot}507}{17{\cdot}755}=2{\cdot}507$, $\frac{L'n}{R}=\frac{39{\cdot}227}{17{\cdot}755}=2{\cdot}212$.

It is not difficult to deduce Lord Kelvin's formula for R'/R from (24); we see, from (19), that

$$\frac{R'}{R}=\frac{P_2}{P_3}=\frac{2z}{r}\left(M\frac{\partial N}{\partial r}-N\frac{\partial M}{\partial r}\right)\Big/\left\{\left(\frac{\partial M}{\partial r}\right)^2+\left(\frac{\partial N}{\partial r}\right)^2\right\}.$$

To compare with Kelvin's actual formulæ, we must express the differentiations in terms of x; and using (3), this gives †

$$\frac{R'}{R}=\frac{x}{2}\left(M\frac{\partial N}{\partial x}-N\frac{\partial M}{\partial z}\right)\Big/\left\{\left(\frac{\partial M}{\partial x}\right)^2+\left(\frac{\partial N}{\partial x}\right)^2\right\},$$

where $M=\mathrm{ber}\,x, \quad N=\mathrm{bei}\,x.$

A table, calculated by Dr. Magnus MacLean, is given in Lord Kelvin's paper and will be found in Prof. Fleming's book (*loc. cit.* p. 103). As an example we may take $x=4$, for which $z=4$; then (15) and (16) give

$$P_2=4{\cdot}2229, \quad P_3=2{\cdot}5168,$$

so that $P_2/P_3=1{\cdot}6779$, while the tabular value is $1{\cdot}6778$.

An alternative method, when $|z|$ is large, is to use the asymptotic formula for I_0, namely ‡

$$I_0(qa)=\frac{e^{qa}}{\sqrt{2\pi qa}}\left\{1+\frac{1}{8qa}+\frac{1.9}{2(8qa)^2}+\ldots\right\}.$$

* Papers, vol. ii. p. 98; they are naturally equivalent to Lord Kelvin's, but they are more simple to work with.

† Lord Kelvin, Math. and Phys. Papers, vol. iii. p. 491; see also Prof. J. A. Fleming, 'Electric Wave Telegraphy,' 4th ed. p. 101 (1919); and Pidduck's 'Electricity,' 2nd ed. p. 399 (it is perhaps useful to note that the table given in the first edition is erroneous).

‡ Other methods are given in § 6 below; I originally devised these in 1908–1909, but they may have been used earlier by Heaviside.

Then, by logarithmic differentiation, we see that

$$\frac{I_1(qa)}{I_0(qa)} = 1 - \frac{1}{2qa} - \frac{\dfrac{1}{8(qa)^2} + \dfrac{9}{64(qa)^3} + \ldots}{1 + \dfrac{1}{8qa} + \dfrac{9}{128(qa)^2} + \ldots}.$$

Thus *, on taking the reciprocal, we see that

$$\frac{qa}{2}\frac{I_0(qa)}{I_1(qa)} = \frac{qa}{2}\left\{1 + \frac{1}{2qa} + \frac{3}{8(qa)^2} + \frac{3}{8(qa)^3} + \ldots\right\}, \quad (25)$$

and proceeding as before, we find that if

$$qa = s(1+\iota), \quad \text{or} \quad s = \sqrt{2z} = \sqrt{2\mu n/R}, \quad . \quad (26)$$

then (22), (23), and (25) give

$$\left.\begin{aligned} \frac{R'}{R} &= \frac{s}{2} + \frac{1}{4} + \frac{3}{32s} + O\left(\frac{1}{s^3}\right) \\ \frac{L'n}{R} &= \frac{s}{2} - \frac{3}{32s} - \frac{3}{32s^2} + O\left(\frac{1}{s^3}\right) \end{aligned}\right\}. \quad . \quad . \quad (27)$$

Although (25) was known to Heaviside † at a later date, yet he never seems to have used more than the first terms in (27)—which constitute the extremely rough approximation due to Lord Rayleigh.

For example, with $z=10$, we have $s=\sqrt{20}=2\sqrt{5}$, and so (27) gives

$$\frac{R'}{R} = \sqrt{5} + \frac{1}{4} + \frac{3}{320}\sqrt{5}, \text{ nearly}$$

$$= 2{\cdot}236 + {\cdot}25 + {\cdot}021 = 2{\cdot}507.$$

while $$\frac{L'n}{R} = \sqrt{5} - \frac{3}{320}\sqrt{5} - \frac{3}{640},$$

to the same order $$= 2{\cdot}236 - {\cdot}021 - {\cdot}005 = 2{\cdot}210.$$

These two values agree extremely well with those found from (24) above ‡.

Similarly, with $z=20$, $s=10\sqrt{2}=14{\cdot}142$, and then we find that

$$R'/R = 7{\cdot}071 + {\cdot}25 + {\cdot}006 = 7{\cdot}327,$$

while the value 7·325 is found in Kelvin's table.

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* See, for instance, my book on 'Infinite Series' (2nd ed.) Art. 117. For more details see § 6 below.

† 'Electromagnetic Theory,' vol. iii. p. 371. (See § 6 below.)

‡ This example was given by Heaviside (Papers, vol. ii. p. 99), but he found a discrepancy through using the rough approximation of Rayleigh, $R'=L'n=(2{\cdot}236)R$, corresponding to the first terms in (27).

§ 4. Lord Kelvin's method of evaluating R′.

This depends on a different physical principle; it is of some historical interest, and affords a useful check, although longer (and less fundamental) than Heaviside's method *.

Let E_3, w denote the electric force and current parallel to the axis; then the rate of heating (per unit length) is

$$\int_0^a E_3\overline{w} \cdot 2\pi r\, dr,$$

where $\overline{w}$ is the complex conjugate to w.

Now, if H_2 is the magnetic force (in circles round the axis) we have

$$4\pi r w = \frac{\partial}{\partial r}(rH_2), \qquad 4\pi r\overline{w} = \frac{\partial}{\partial r}(r\overline{H}_2), \qquad \text{and} \qquad \mu p H_2 = \frac{\partial E_3}{\partial r}.$$

Using these results, we can integrate by parts, and then the formula for the rate of heating becomes

$$\frac{1}{2}\Big[rE_3H_2\Big]_0^a - \frac{1}{2}p\int_0^a \mu H_2\overline{H}_2\, dr.$$

The last term gives zero *on the average*, since it is a perfect differential with respect to t; thus we can take the rate of heating as the time-average of

$$\tfrac{1}{2}a(E_3\overline{H}_2)_{r=a}.$$

Now, at $r=a$, we have

$$E_3 = (R' + L'p)C, \qquad \text{and} \qquad 2\pi a\overline{H}_2 = 4\pi\overline{C},$$

where C is the total current and $\overline{C}$ is its conjugate complex.

Thus our result is the average of $(R'+L'p)(C\overline{C})$, and so the final estimate of the effective resistance is again equal to R′.

§ 5. *The correlated problem of a coil surrounding a central core.*

It is proved by Heaviside † that the effective resistance and self-inductance are then given by

$$R_1' + L_1'p = L_1 p \left\{ \frac{2I_1(qa)}{qaI_0(qa)} \right\},$$

* It is perhaps necessary to caution readers against the version of this method given on pp. 102, 103 of Prof. Fleming's book: the slip made there is often to be found in energy-calculations when complex variables are used to represent the electric and magnetic fields. The fallacy lies in the assumption that the square of the intensity is equal to the square of the corresponding complex; but it is evident that (x^2+y^2) is far from being equal to $(x+iy)^2$, and the former is not even equal to the real part of the latter.

When the square of the intensity is needed, it is necessary to multiply the complex by its *conjugate*; that is, $(x+iy)$ by $(x-iy)$ gives x^2+y^2.

† See, for instance, Papers, vol. ii. p. 99; as a matter of rapid calculation we can obtain all the necessary results (except for small points of detail) by an interchange of the electric and magnetic fields in § 1.

the expression in brackets simply being the reciprocal of that used in the original problem.

Now, in the notation used before, this bracket is equal to

$$\begin{aligned}\frac{4}{(qa)^2}\frac{u'}{u} &= \frac{1}{2\iota z}\left\{\left(\frac{u'}{u}+\frac{v'}{v}\right)+\left(\frac{u'}{u}-\frac{v'}{v}\right)\right\}\\ &= \frac{1}{2\iota z}\left(\frac{z^2\mathrm{P}_4}{\mathrm{P}_1}+2\iota\frac{z\mathrm{P}_2}{\mathrm{P}_1}\right)\\ &= \frac{\mathrm{P}_2}{\mathrm{P}_1}+\frac{z\mathrm{P}_4}{2\iota\mathrm{P}_1} \quad \ldots\ldots\ldots \quad (28)\end{aligned}$$

Writing $p=\iota n$ as before, we see that now

$$\frac{\mathrm{R}_1'}{\mathrm{L}_1 n}=\frac{z}{2}\frac{\mathrm{P}_4}{\mathrm{P}_1}, \qquad \frac{\mathrm{L}_1'}{\mathrm{L}_1}=\frac{\mathrm{P}_2}{\mathrm{P}_1}, \quad \ldots\ldots \quad (29)$$

which agree with Heaviside's formulæ (91h) and (92h).

When $|z|$ is large, we can replace (28) by a formula corresponding to (25), which gives

$$\frac{2\mathrm{I}_1(qa)}{qa\mathrm{I}_0(qa)}=\frac{2}{qa}\left\{1-\frac{1}{2qa}-\frac{1}{8(qa)^2}-\frac{1}{8(qa)^3}-\ldots\right\}. \quad (30)$$

Then, if we write, as in (26), $qa=s(1+\iota)$, the formula (30) becomes

$$-\frac{\mathrm{LR}_1'}{\mathrm{L}_1 n}+\frac{\mathrm{L}_1'}{\mathrm{L}_1}=\frac{1-\iota}{s}-\frac{1}{2\iota s^2}+\frac{1+\iota}{16s^3}+\frac{1}{16s^4}+\ldots. \quad (31)$$

It follows that

$$\left.\begin{aligned}\frac{\mathrm{R}_1'}{\mathrm{L}_1 n}&=\frac{1}{s}-\frac{1}{2s^2}-\frac{1}{16s^3}+\mathrm{O}\left(\frac{1}{s^5}\right)\\ \frac{\mathrm{L}_1'}{\mathrm{L}_1}&=\frac{1}{s}+\frac{1}{16s^3}+\frac{1}{16s^4}+\mathrm{O}\left(\frac{1}{s^5}\right)\end{aligned}\right\}. \quad \ldots \quad (32)$$

As an illustration we may take, as before, $z=10$, $s=\sqrt{20}=2\sqrt{5}$, for which we find that

$$\mathrm{P}_1=198{\cdot}2, \qquad \mathrm{P}_2=44{\cdot}507, \qquad \mathrm{P}_4=7{\cdot}8454.$$

Then (29) gives the values

$$\frac{\mathrm{R}_1'}{\mathrm{L}_1 n}=\frac{39{\cdot}227}{198{\cdot}20}={\cdot}1979, \qquad \frac{\mathrm{L}_1'}{\mathrm{L}_1}=\frac{44{\cdot}507}{198{\cdot}20}={\cdot}2245.$$

And from (32) we find that

$$\begin{aligned}\frac{\mathrm{R}_1'}{\mathrm{L}_1 n}&=\frac{1}{2\sqrt{5}}\left(1-\frac{1}{320}\right)-\frac{1}{40}={\cdot}2229-{\cdot}0250={\cdot}1979,\\ \frac{\mathrm{L}_1'}{\mathrm{L}_1}&=\frac{1}{2\sqrt{5}}\left(1+\frac{1}{320}\right)+\frac{1}{6400}={\cdot}2243+{\cdot}00016={\cdot}2245.\end{aligned}$$

§ 6. **Asymptotic series for use when $|qr|$ is large.**

These formulæ are due (probably) to Heaviside ; the first place in which they occur in a complete form is in his 'Electromagnetic Theory,' vol. iii. p. 371.

In the first place, no confusion with § 2 need arise if we write x for what is there called qr; so that x is now a complex number (of phase $\frac{1}{4}\pi$). Then*

$$\mathrm{I}_0(x)=\frac{1}{\sqrt{2\pi x}}\left[e^x\left\{1+\frac{1}{8x}+\frac{1\cdot 9}{2\,!\,(8x)^2}+\dots\right\}\right.$$
$$\left.+\iota e^{-x}\left\{1-\frac{1}{8x}+\frac{1\cdot 9}{2\,!\,(8x)^2}+\dots\right\}\right],$$

the sign of ι in the second term being positive, since the imaginary part of x is also positive.

In order to obtain a formula for $\mathrm{I}_0(x)/\mathrm{I}_1(x)$ which is of a reasonable type, we must restrict x so that the second term is small compared with the first.

This requires that $e^{-2\xi}$ shall be small where $x=\xi(1+\iota)$; for a relative order of 1/1000, $\xi\geqq 3{\cdot}5$, and so $|x|\geqq 5$, say; for the order 1/10,000, we take $\xi\geqq 4{\cdot}6$ and $|x|\geqq 7$ (roughly).

It is then evident that expansions in descending powers of x of the types used in (25) and (30) are *possible* : to find the sequence of coefficients, write

$$u=\mathrm{I}_0(x)/\mathrm{I}_1(x), \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where again there is no risk of confusion with the former u. Then it is easy to verify that

$$\frac{du}{dx}=1+\frac{u}{x}-u^2=1+\frac{1}{4x^2}-\left(u-\frac{1}{2x}\right)^2. \quad . \quad (34)$$

Thus, if we try the series

$$u=1+\frac{1}{2x}+\frac{\mathrm{A}_2}{x^2}+\frac{\mathrm{A}_3}{x^3}+\dots,$$

we find from (34), the identity

$$\frac{1}{2x^2}+\frac{2\mathrm{A}_2}{x^3}+\frac{3\mathrm{A}_3}{x^4}+\frac{4\mathrm{A}_4}{x^5}+\dots$$
$$=-\left(1+\frac{1}{4x^2}\right)+\left(1+\frac{\mathrm{A}_2}{x^2}+\frac{\mathrm{A}_3}{x^3}+\dots\right)^2.$$

* See, for instance, my 'Infinite Series,' 2nd ed. p. 353 ; the result is due to Stokes. But it should be noted that in the formula given for $\mathrm{I}_n(x)$ in my book, n must be an integer.

Thus

$$\tfrac{1}{2}=-\tfrac{1}{4}+2A_2,\quad 2A_2=2A_3,\quad 3A_3=2A_4+A_2^2,$$
$$4A_4=2A_5+2A_2A_3,\quad 5A_5=2A_6+2A_2A_4+A_2^2\ldots\ldots,$$

or $$A_2=\frac{3}{8},\quad A_3=\frac{3}{8},\quad A_4=\frac{63}{128},\quad A_5=\frac{27}{32},\quad .\quad (35)$$

and in addition, $A_6=\frac{949\frac{1}{2}}{512}$ (as given by Heaviside).

Similarly, if we write $v=1/u$ in the equation (34), we find that

$$\frac{dv}{dx}=1-\frac{v}{x}-v^2\qquad v=1-\frac{1}{2x}-\frac{B_2}{x^2}-\frac{B_3}{x^3}-\ldots,\quad (36)$$

and so

$$\frac{1}{2x^2}+\frac{2B_2}{x^3}+\frac{3B_3}{x^4}+\frac{4B_4}{x^5}+\ldots$$
$$=1+\frac{1}{4x^2}-\left(1-\frac{B_2}{x^2}-\frac{B_3}{x^3}-\ldots\right)^2.$$

Thus

$$\tfrac{1}{2}=\tfrac{1}{4}+2B_2,\quad 2B_2=2B_3,\quad 3B_3=2B_4-B_2^2,$$
$$4B_4=2B_5-2B_2B_3,\quad 5B_5=2B_6-2B_2B_4-B_3^2\ldots\ldots,$$

so that $$B_2=\frac{1}{8},\quad B_3=\frac{1}{8},\quad B_4=\frac{25}{128},\quad B_5=\frac{13}{32},\quad .\quad (37)$$

and apparently * $$B_6=\frac{536\frac{1}{2}}{512}.$$

LXXXV. *On the Investigation of Predischarges.*

[Plate XIV.]

To the Editors of the Philosophical Magazine.

Gentlemen,—

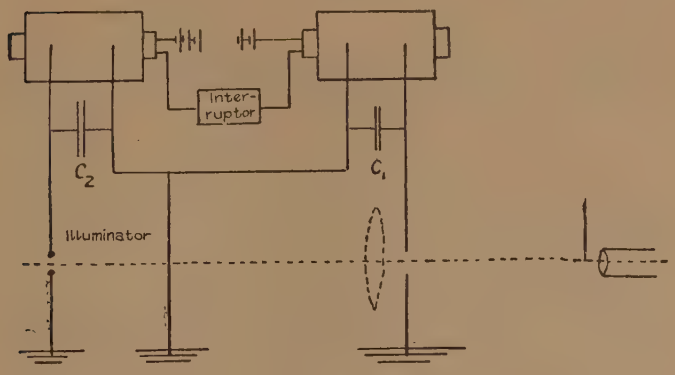
In the May number of the Phil. Mag. [7] v. p. 1698 (1928), Prof. Harvey A. Zinszer, Hanover College, writes that the "Schlieren" method of Toepler and Mach has not been made use of hitherto in the investigation of the life-history of the spark. He is also of opinion that the

* The last coefficient is given by Heaviside as $\frac{69}{64}=\frac{552}{512}$; but I have checked the value given above in other ways.

"Schlieren" method as employed by Toepler, Mach, and Wood is not qualified for the investigation on the life-history of the spark.

Already in 1922 I published * photographs of brush-discharge "Schlieren," and showed that the "Schlieren" method has been useful in giving more precise information about the life-history of the spark. I believe that I have reason to say that by the dispositions of Toepler and Wood I got pictures which, in spite of their smallness, render the most subtle details more sharply than the shadow method of Foley, which has been used by Prof. Zinszer. Therefore I send you three photographs (Pl. XIV. figs. 1–3) with the request to publish them in your Magazine.

Fig. 4.



The Experimental Disposition.—The "Schlieren" apparatus was set up and adjusted in the usual manner described by Toepler. But to obtain a delay between the illumination-spark and the discharge to be examined, a method was employed which differs from those made hitherto by Toepler and Mach for photography of sound-waves. By an oscillatory discharge in the oscillatory circuit of the sound-spark the tension of the illumination-spark is considerably raised in a wholly determined phase of the first oscillatory circuit, and thus led Toepler and Mach to the installation of the illumination-spark in a fixed interval of time after the sound-spark. But this method is not adaptable for the investigation of pre-discharges, where the well-defined oscillations are wanting. Therefore I used two big inductors (fig. 4), and fastened their primary spools one after the

* *Phys. Zeitschr.* xxiii. p. 193 (1922).

other to the same interrupter. The condenser of the interrupter had to be enlarged correspondingly, so that the light arc of the interrupter was small and short. At every interruption of the primary circuit both secondary spools receive a shock by which the capacities C_1 and C_2 lying near them are charged. According to the period of the oscillatory circuit T_1 and T_2, which depend on the self-inductions of the secondary spools and the capacities C_1 and C_2, the one discharge will take place earlier than the other one.

Besides the two pointed electrodes (left +, right −) and the "Schlieren," some light equidistant lines are to be seen on the photographs (Pl. XIV. figs. 1–3). They are caused by the diffraction of the light by thin threads of quartz, which are spread before the lens at the distance 1 cm. from one another, so that the dimensions of the discharge may be easily read.

Results of the Observation.—The experiments were undertaken in order to determine which of the predischarges, the positive or the negative, is the more important for long sparks. Therefore the experiments always began with sparks, and then only passed over to predischarges by means of magnifying the electrode distance. Upon the illustrations we can see distinctly that the discharge under the given experimental conditions consists principally of a positive brush discharge. The negative part of the discharge is upon all photographs very much smaller, on the average about six times smaller, than the positive one. The middle length of the positive brush discharges amounted to 2·4 cm. at the tension of 32–35 kilovolts and an electrode distance of 5 cm. The middle length of the negative discharge is only 4 mm.; besides, the longest positive discharge was 5·5 cm. long and the longest negative only 1·0 cm. For the calculation of the middle length, only such plates were taken on which positive and negative "Schlieren" were to be seen simultaneously; 105 such photographs were obtained. It can further be demonstrated that by a change of the tension the length of the positive part of the discharge is more influenced than the length of the negative part.

Finally it may be mentioned that on moving plates, if several oscillations of the illumination-spark are employed, we can observe the temporal change of the discharge "Schlieren." The time-intervals can be estimated by the velocity of the plates. By this manner it could be fixed that the "Schlieren" rendered on figs. 1–3 (Pl. XIV.) had been

taken about $4–8 . 10^{-4}$ sec. after the discharge. After $1 . 10^{-3}$ sec. the "Schlieren" pictures were already indistinct, and after $2 . 10^{-3}$ sec. nothing at all was to be distinguished.

Results.—By means of brush-light "Schlieren" it is demonstrated that with the long sparks—where the electrode distance is much larger than the radius of curvature of the electrodes—the spark track is produced by the positive pre-discharge.

Yours faithfully,

Riga University.
June 20, 1928.

Fr. Trey,
Dr. Phil.

LXXXVI. *Electrical Properties of Neon.* *By* J. S. Townsend, *M.A., Wykeham Professor of Physics, Oxford, and* S. P. MacCallum, *M.A., Fellow of New College, Oxford* *.

1. THE experiments on the electrical properties of neon and helium which were made in the Electrical Laboratory, Oxford, have shown that in the development of large currents the photoelectric effect of radiation from the gas is very small compared with the effect of ionization by collision †, but the apparatus used in those experiments was not suitable for the determination of the coefficients α and β, which occur in the formula for the rate of increase of the current with the distance between the electrodes in a uniform electric field.

A new type of apparatus (fig. 1) with parallel plates was therefore made to determine the coefficients α and β, which also provided a means of comparing the effect of the radiation from the gas with other processes of ionization.

It was found to be of considerable advantage to have the apparatus enclosed in a long transparent envelope, so that a high frequency discharge could be used to examine the spectrum of the gas and to remove impurities.

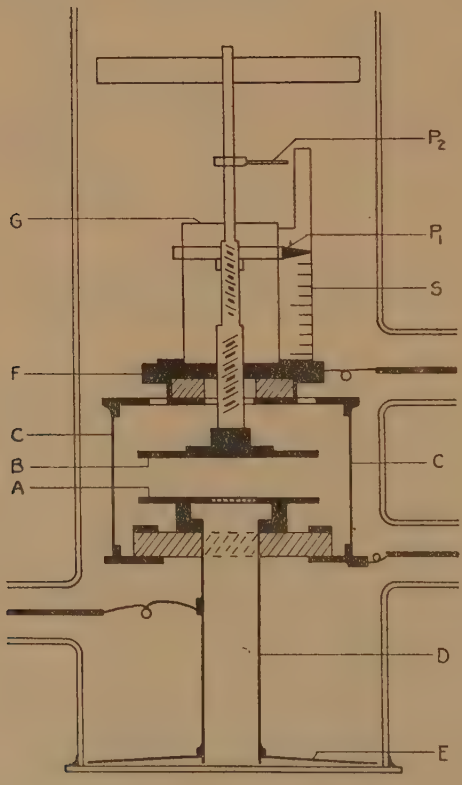
A quartz cylinder 23 cm. long and 5·8 cm. in diameter was therefore used to contain the apparatus. Flat quartz plates were fused to the ends of the cylinder, and the ultraviolet light from an external spark gap was introduced

* Communicated by the Authors.

† J. S. Townsend and C. M. Fochen, Phil. Mag. ii. (Aug. 1926).

through the lower quartz plate, as shown in figs. 1 and 2. All the metal parts were of nickel, except the small bar magnet which was used to rotate the micrometer screw, and the molybdenum rods with the lead seals in the side tubes for connecting to the electrodes.

Fig. 1.



The quartz side tubes and lead seals were made very carefully by Messrs. Mullard, and the joints were perfectly air tight.

It was thus possible to heat the apparatus to a high temperature to remove impurities from the quartz and metal surfaces. The experiments * on the effect of the high frequency discharge in removing small traces of im-

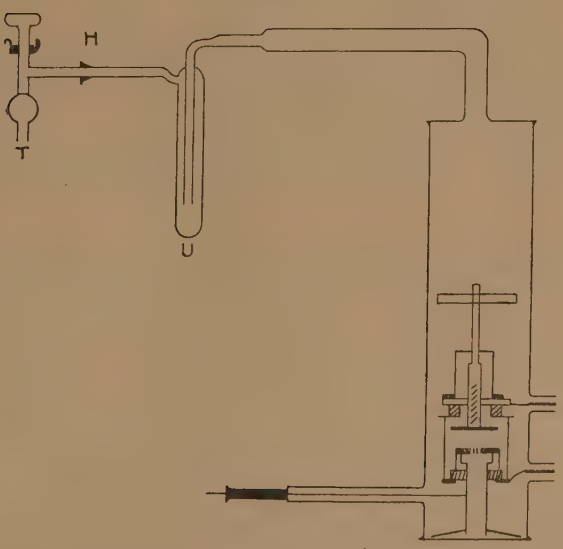
* J. S. Townsend and S. P. MacCallum, Phil. Mag. v. p. 695 (April 1928).

purities from neon which have already been described, were made with this apparatus.

The effects of small traces of impurities on the sparking potentials in diatomic gases have been determined by Meyer * and Dubois †. Many experiments on this subject are described in a recent paper by Prey ‡.

2. The arrangement of the electrodes is shown in fig. 1. They consisted of two parallel plates A and B, 3·5 cm. in diameter, and a cylinder C 4·5 cm. in diameter; a grid was formed by a set of parallel saw cuts ·5 mm. wide and

Fig. 2.



1 mm. apart in the centre of the lower plate, through which the ultra-violet light passed and fell on the upper plate. A tube D about 6 cm. long and 1·2 cm. in diameter was screwed to the base of the plate A, and a thin plate E, 5·2 cm. in diameter, was screwed over the lower end of the tube.

The ultra-violet light from the external spark gap passed through the tube to the grid in A, and the cylinder C was screened from the light by the plate E.

* E. Meyer, *Ann. de Phys.* lviii. p. 297 (1919), and lxv. p. 335 (1921).
† E. Dubois, *Ann. de Phys.* (9) xx. (Sept. and Oct.) 1923.
‡ B. Prey, *Ann. de Phys.* lxxxv. p. 381 (1928).

The base of the plate A was fixed to quartz rods of rectangular section, and the ends of the rods were fixed to a flange on the lower end of the cylinder C.

The upper plate B was fixed to a spindle with a micrometer screw of one millimetre pitch, which rotated in a threaded hole in the metal plate F. The upper part of the spindle was reduced so as to pass freely through a small guiding hole in the cross-piece G, which was fixed to F. A short rod of soft iron was fixed to the upper end of the spindle, and the distance between the plates was adjusted by turning the iron rod with a horseshoe magnet.

The metal plate F was mounted on two quartz rods, the ends of the rods being fixed to a flange on the upper part of the cylinder C.

The four quartz rods supporting the two parallel plate electrodes were firmly clamped in positions adjusted so as to have the two plates exactly parallel.

The distance between the plates was given by a pointer P_1 on the scale S. The pointer was fixed to a small metal plate with a screw thread fitting a left-handed screw on the upper part of the spindle between F and G. Thus for one revolution of the spindle the plate B moved one millimetre, while the pointer moved two millimetres, so that the divisions of the scale were two millimetres apart and were easily seen through the quartz cylinder. The pointer P_2 was fixed to the spindle, and the distance between A and B was adjusted exactly by setting P_2 in a certain position.

The connexions to the plates A and B and the cylinder C were made with molybdenum rods through long quartz side tubes with lead seals.

All the metal parts were carefully cleaned and heated to a temperature of 500° C. in a vacuum before being assembled.

3. When fixed in position in the quartz cylinder the metal plate E rested on the quartz plate that closed the end of the cylinder, as shown in fig. 2. A quartz tube about 1·2 cm. in diameter was sealed in the upper end of the cylinder, and led through a pair of coaxial quartz tubes U to the tap T. The quartz and glass tubing were connected by a ground joint H, which was made air tight with a hard elastic cement.

The arrangement of the apparatus used to purify the gas, comprising a quartz tube containing copper oxide with an electric heater and a glass tube containing charcoal cooled with liquid air, has been described in the accounts of other

experiments which were made in the laboratory with helium and neon *.

The pure gas was admitted to the apparatus through the tap T (fig. 2), and it was intended to cool the tubes U with liquid air in order to prevent impurities from diffusing into the tap. This, however, was not found to be of much advantage. If charcoal is used in the tubes the neon is slowly absorbed when the tubes are cooled, so that in making experiments at different pressures time is wasted in waiting for the pressure to become steady. Without charcoal there is no appreciable change in the electrical properties for one or two days, when the tubes are kept cool with liquid air. When the tubes were not cooled a small change was observed after the gas had been five or six hours in the apparatus, but the amount of impurity was so small that it could be completely removed in less than one minute by a high frequency discharge in the upper part of the cylinder. This method of purifying the gas was found to be effective in removing the amount of impurity that accumulates in the gas after being one or two days in the apparatus.

4. The calculations of the ionization coefficients α and β are greatly simplified when the sparking potential V is known in terms of the product of the gas pressure p and the distance S between the plates.

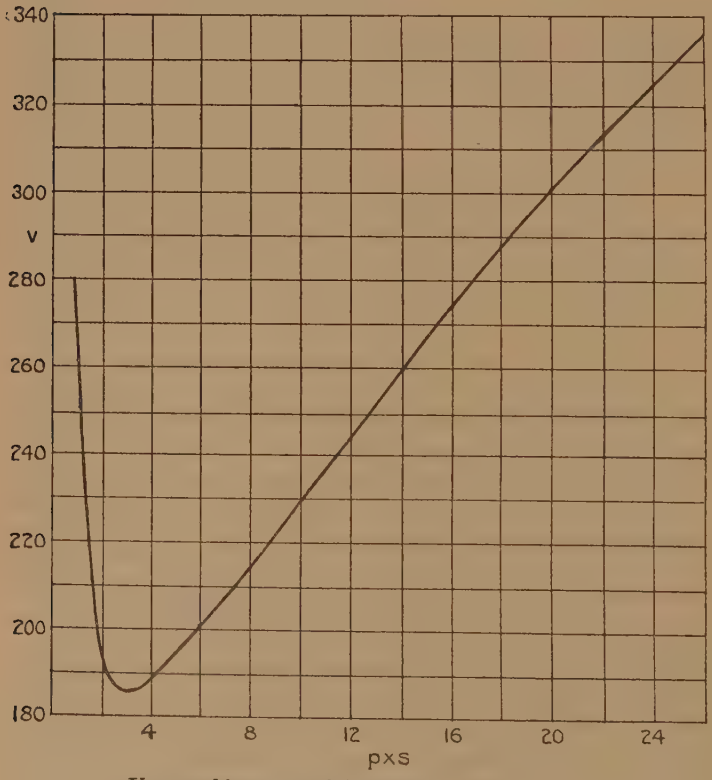
A battery of small accumulators was used to determine the potentials with a potentiometer to adjust the potential to one fifth of one volt. The connexions to the plates were made through high resistances with a galvanometer in one of the lines. The cylinder C may be insulated or connected to a point of the battery where the potential is nearly midway between the potentials of the plates. The current in the gas was observed either by the galvanometer or by the glow in the gas which was seen through a narrow slit in the cylinder C. A set of measurements were made with the plates 5 mm. apart and with 36 different pressures of the gas from 1·8 to 52 mm. The experiments were made with different specimens of pure gas within one or two hours after the gas was admitted to the apparatus. In these cases no change was observed in the sparking potential after the high frequency discharge was passed through the gas in the upper part of the quartz cylinder. The same values of V were obtained, generally within half a volt, with

* J. S. Townsend and C. M. Fochen, Phil. Mag. ii. p. 474 (August 1926); H. G. L. Huxley, Phil. Mag. v. p. 721 (April 1928).

other specimens of gas that were used in the course of the investigations. The results of these experiments are given by the curve (fig. 3), where the ordinates are the values of V in volts, and the abscissæ the product of the pressure p and the distance S between the plates.

The experiments which have been quoted * in describing the effect of the high frequency current in removing

Fig. 3.



V = sparking potential in neon in volts.
p = pressure of gas in millimetres.
S = distance between the plates in centimetres.

impurities from the gas, indicate the degree of accuracy that may be obtained in measurements of the sparking potentials with different specimens of the gas. The results taken from a curve drawn on a large scale are given in

* J. S. Townsend and S. P. MacCallum, *loc. cit.*

Table I. for definite values of the product $p \times S$ above and below the point of minimum sparking potential, which was 186 volts near the point where $p \times S = 3$. The ratio $X/p = V/(p \times S)$ is given in the third column of the table.

TABLE I.

Neon.—Sparking potentials for parallel plates.

$p \times S$.	V.	X/p.	$p \times S$.	V.	X/p.
26	336	12·9	6	202	33·7
24	325	13·5	5	194	38·8
22	313	14·2	4	189	47·2
20	301	15·0	3	186	62·0
18	288	16·0	2·5	187	75
16	274	17·1	2·0	194	97
14	260	18·6	1·6	206	129
12	244	20·3	1·2	236	197
10	229	22·9	1·0	271	271
8	214	26·7			

5. No change was observed in the sparking potential with a fresh quantity of pure gas after it had been in the apparatus for a few hours, but after one or two days there was a change of several volts. This was due to an impurity, in an amount so small that in most cases it could not be observed in the spectrum of the high frequency discharge. Occasionally a slight discoloration of the glow was noticed for one or two seconds after the discharge was started, but the discharge acts so quickly in removing the impurity that after about half a minute all traces disappear and the sparking potential is brought back to the value obtained with the pure gas and remains at that value for two or three hours.

The high frequency discharge thus provides a simple means of removing small traces of impurities, and the gas used in an experiment may be tested by finding the sparking potential before and after a high frequency discharge is passed through the gas.

As a rule the tubes U were not cooled with liquid air, and no experiments were made with gas that had been in the apparatus for more than two days, as the impurity is not

completely removed by the high frequency discharge when it is allowed to accumulate for long periods. In these cases the quartz cylinder was heated and the gas was pumped out while the apparatus was hot, and washed out once or twice with pure gas before making measurements.

It is necessary to have gas at a considerable pressure, about 10 or 20 mm., in the apparatus when the quartz cylinder is heated, in order to conduct the heat to the electrodes, otherwise some impurity may be driven on to the electrodes.

When these precautions were observed very consistent results were obtained. The experiments were frequently repeated with different specimens of gas, and there was no disagreement in the results greater than the errors that occur in measuring the electrometer currents or in reading the pressures with ordinary gauges.

6. In determining the photoelectric currents, the upper plate was connected to an electrometer with a set of condensers of small capacity to form an induction balance in order to maintain the plate close to the zero potential while the current was flowing. The lower plate was connected to the positive terminal of a battery of small accumulators, the negative terminal being connected to earth. The cylinder C was maintained at a fixed potential by connecting it to earth or to a point of the battery where the potential was less than half that of the lower plate.

The photoelectric currents n were measured with a constant electric force X and different distances x between the plates. The electrons set free from the upper plate by ultra-violet light from an external spark gap acquire energy as they move in the direction of the electric force, and after a certain point the atoms of the gas are ionized and the current increases continuously with the distance x. This effect takes place gradually, and there are no points at which the current changes abruptly until the sparking distance S corresponding to the force X is reached.

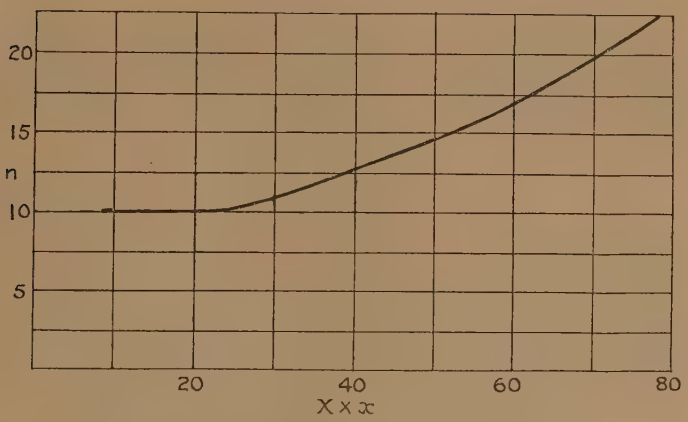
The initial stages of the process of ionization by collision may be observed with a force of 100 volts per centimetre and distances from 2 to 7 mm. between the plates. With this force the largest increases in current are obtained with a pressure of about 2·5 mm. In this case [$p = 2{\cdot}5$, $X = 100$] the increase in current is about one per cent. of n_0 [the number of electrons set free per second by the ultra-violet light] when the plates are 2 mm. apart, and the potential of the lower plate 20 volts, but the current

does not attain the value $2n_0$ until the plates are about 7 mm. apart where the potential is 70 volts.

For a given value of the ratio of the electric force X to the gas pressure p the ratio n/n_0 depends only on the potential $x \times X$, and for each value of the ratio X/p the currents may be represented in terms of the potentials by a curve.

The curve corresponding to the case where $X/p = 30$ is given in fig. 4, the ordinates being the currents n and the abscissæ the potentials $X \times x$ in volts, the ordinate corresponding to n_0 being taken as 10. Thus, if the force were

Fig. 4.



Photoelectric currents in neon [$X/p = 30$].
X in volts per centimetre, x in centimetres.

100 volts per centimetre and the pressure 3·3 mm., the ratio n/n_0 would be 1·8 when the plates are 6·3 mm. apart and the potential 63 volts.

The rate of increase of the current in the initial stages, where n/n_0 is less than 2 for different values of the ratio X/p, is indicated by the ratios N_6/N_2 given in Table II. The current N_2 was obtained with plates 2 mm. apart and the potential 20 volts, and N_6 with plates 6 mm. apart and the potential 60 volts with the gas at different pressures p. The ratio X/p is given in the last column of the table, X being 100 volts per centimetre, and p the pressure in millimetres of mercury.

TABLE II.

X = 100 volts per centimetre.

p.	N_6/N_2.	X/p.	p.	N_6/N_2.	X/p.
7·35	1·43	13·6	1·61	1·71	62
6·50	1·48	15·4	1·165	1·60	86
5·54	1·54	18·1	·772	1·45	129
4·30	1·64	23·3	·633	1·38	158
3·32	1·73	30·1	·520	1·30	192
2·30	1·78	43·5			

7. When the electrons have traversed a certain distance x' in the direction of the electrical force the currents obtained with a constant electric force and a constant gas pressure are given in terms of the distance x between the plates by the formula

$$n = \frac{n_0(\alpha-\beta)\epsilon^{(\alpha-\beta)(x-\delta)}}{\alpha-\beta\epsilon^{(\alpha-\beta)(x-\delta)}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for distances from x' to S, where S is the distance at which a spark is obtained.

Within this range the electrons and positive ions attain a steady motion, in which α and β are constant and independent of x. The lower limit x' is greater than the distance δ that occurs in the formula, but it is not a sharply defined point and it depends on the pressure of the gas.

If 2 mm. be taken as the shortest distance between the plates at which the currents are measured, the values of n are in agreement with the above formula for the range of distances from $x = \cdot2$ to $x = S$, with pressures greater than 1·5 mm., when the electric force is 350 volts per centimetre. Somewhat smaller pressures may be taken with smaller forces, but if the pressure be reduced to one millimetre the currents with the plates 2 mm. apart are not in accordance with the formula, even with forces as low as 250 volts per centimetre.

In order to obtain the constant values of α and β the plates must be at distances such that the product $p \times x$ is greater than ·3.

In neon there is no considerable range of distances where the current is given approximately by the formula $n = n_0\epsilon^{\alpha x}$, which shows that the coefficient β is not very small compared with α. With this gas the simplest method of finding

α/p and β/p in terms of X/p is to determine $(\alpha-\beta)$ and the ratio $\beta/(\alpha-\beta)$ from measurements of the currents.

Equation (1) may be written in the form

$$n = n_0 \frac{\epsilon^{(\alpha-\beta)(x-\delta)}}{1+\gamma-\gamma\epsilon^{(\alpha-\beta)(x-\delta)}}, \quad . \quad . \quad . \quad . \quad (2)$$

where $\gamma=\beta/(\alpha-\beta)$, and since n/n_0 is infinite when x is the sparking distance S, the following relation between δ and S is obtained :

$$(1+\gamma)\epsilon^{(\alpha-\beta)\delta} = \gamma\epsilon^{(\alpha-\beta)S},$$

so that equation (2) becomes

$$n = \frac{n_0}{\gamma} \times \frac{1}{\epsilon^{(\alpha-\beta)(S-x)}-1}. \quad . \quad . \quad . \quad . \quad (3)$$

This equation shows that $(\alpha-\beta)$ may be found from measurements of the ratios of the currents n, but in order to determine γ it is necessary to determine the ratio n/n_0 of a current n in the range from x' to S to the current n_0 due to electrons set free from the negative electrode by the ultra-violet light from the external spark gap.

8. Let n_a, n_b, n_c be three currents obtained with a constant electric force X and constant pressure p, with the distances a, b, and c between the plates where $(b-a) = (c-b)$. Three equations are thus obtained, from which n_0/γ and S, which occur in equation (3), may be eliminated and the following formula for $(\alpha-\beta)$ is obtained :

$$\epsilon^{(\alpha-\beta)(a-b)} = \frac{y_2(y_1-1)}{(y_2-1)}, \quad . \quad . \quad . \quad . \quad (4)$$

where y_1 is the ratio n_b/n_a and y_2 the ratio n_c/n_b.

In one set of experiments the currents n_2, n_4, and n_6 were determined with the distances 2, 4, and 6 mm. between the plates, the electric force being 250 volts per centimetre and the gas at pressures from 1·7 to 7·4 mm. The results of the experiments are given in Table III., $(\alpha-\beta)$ being obtained by equation (4) from the ratios n_4/n_2 and n_6/n_4.

The figures in the second and third columns show that the process of ionization represented by the coefficient β has a marked effect even at the distance of 4 mm. between the plates, since the ratios n_6/n_4 are considerably greater than the ratios n_4/n_2. Since the steady motion in which α and β are independent of x is not attained in the distance $x = \cdot2$ with pressures less than 1·6 mm., it is necessary to increase

TABLE III.

X = 250 volts per centimetre.

p.	n_4/n_2.	n_6/n_4.	$\frac{\alpha-\beta}{p}$.	$\frac{X}{p}$.
1·7	2·18	2·66	1·87	147
2·07	2·29	3·03	1·58	120
2·40	2·42	3·40	1·46	104
4·0	2·51	3·73	·92	62·5
5·5	2·41	3·61	·62	45·5
7·4	2·36	3·05	·48	33·8

the electric force in order to obtain the values of $(\alpha-\beta)/p$ that correspond to larger values of X/p.

The results of experiments with the same distances between the plates, 2, 4, and 6 mm., where the force X was greater than 250 volts per centimetre, are given in Table IV., n_4/n_2 and n_6/n_4 being the ratios of the currents.

TABLE IV.

X.	p.	n_4/n_2.	n_6/n_4.	$\frac{\alpha-\beta}{p}$.	$\frac{X}{p}$.
300	1·7	2·50	3·6	2·14	177
300	1·96	2·63	4·7	1·87	153
300	4·4	3·22	15·1	·98	68·2
300	6·0	3·18	13·0	·715	50·0
350	1·68	2·73	5·3	2·25	208
350	2·05	3·10	9·7	2·07	170
350	25	2·12	2·47	·126	14
350	44	1·50	1·59	·035	8
350	50	1·45	1·48	·031	7
420	35	2·21	2·70	·093	12
440	44	1·96	2·34	·060	10
176	44	1·13	1·14	? ·015	4
110	44	1·11	1·12	? ·010	2·5

The experiments with the gas at the pressures from 25 to 50 mm. were made in order to obtain the values of $(\alpha-\beta)/p$ corresponding to small values of the ratio X/p. In these cases it is necessary to have very large pressures as the forces

must be large in order to have large changes in the current when the distance between the plates is changed. A considerable increase in the current with the distance x is obtained with large pressures and small forces as shown by the values n_4/n_2 and n_6/n_4 in the two last experiments recorded in Table IV., but the values of $(\alpha-\beta)$ deduced from them are not accurate, as a small error in the measurement of the current gives rise to a large error in $(\alpha-\beta)$.

9. In order to show that the formula (2) gives the currents up to the distance S, at which a spark is obtained, the electric force was increased so that at the distance c, $X \times c$ is the sparking potential V. In this case $n_c/n_b = \infty$ and equation (4) becomes

$$\epsilon^{(\alpha-\beta)(b-a)} = \frac{n_b}{n_a} - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$(b-a)$ being equal to $(c-b)$ as before.

The last experiment recorded in Table III. where the pressure was 7·4 mm. may be taken as an example to show that the same value of $(\alpha-\beta)$ is obtained over the range of distance from $x=\cdot2$ to $x=\cdot8$. With this pressure the sparking potential is 200 volts when the plates are 8 mm. apart, the electric force being 250 per cm. as in the measurements of the currents n_2, n_4, and n_6.

Thus according to equation (5), $(\alpha-\beta)$ is obtained by the relation

$$\epsilon^{(\alpha-\beta)\times\cdot2} = \frac{n_6}{n_4} - 1 = 2\cdot05,$$

and from the ratios n_4/n_2 and n_6/n_4 equation (4) gives

$$\epsilon^{(\alpha-\beta)\times\cdot2} = \frac{(n_4/n_2-1)}{(n_6/n_4-1)} \times \frac{n_6}{n_4} = 2\cdot02.$$

In most of the experiments in which $X \times c$ was taken as the sparking potential the values of X/p were not the same as those in the above tables.

In one set of experiments the currents n_3 and n_5 were measured with the plates 3 mm. and 5 mm. apart and the force adjusted to the value $V/\cdot7$, V being the sparking potential with the plates 7 mm. apart as given by curve 1. The results of these experiments are given in Table V., the values of $(\alpha-\beta)$ being obtained by the formula (5). In this table p is the pressure of the gas in mm., V the sparking potential in volts corresponding to the product $p \times S = \cdot7 \times p$, and $X/p = V/(\cdot7 \times p)$.

It will be noticed that n_5/n_3 is nearly constant (about 3·2) in these experiments where the currents n_3 and n_5 are measured at the distances 3 S/7 and 5 S/7, the number $2\,S(\alpha-\beta)/7$ as obtained by equation (5) is $\log(2{\cdot}2)$ and $S(\alpha-\beta)$ is thus found to be 2·76 for values of X/p from 13 to 53. This indicates a simple relation between the curves giving $(\alpha-\beta)/p$ in terms of X/p and the sparking potential V in terms of $p\times S$, since $\dfrac{\alpha-\beta}{p}=\dfrac{2{\cdot}76}{p\times S}$ and $X/p=V/pS$.

The results of the various determinations of $(\alpha-\beta)/p$ in terms of X/p given in Tables III., IV., and V., are shown by the lower curve fig. 5, where the ordinates

Table V.

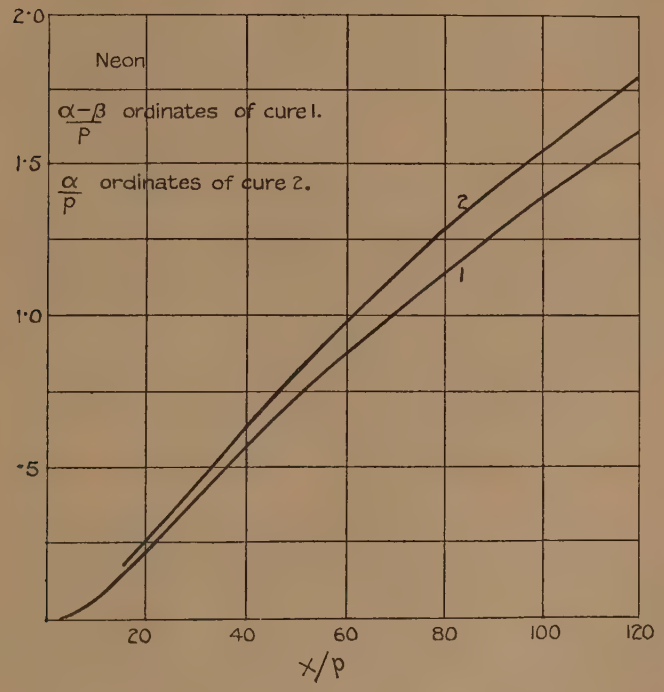
p.	V.	n_5/n_3.	$\dfrac{\alpha-\beta}{p}$.	$\dfrac{X}{p}$.
5	187	3·25	·80	53·5
6·5	191	3·18	·60	42·0
8	198	3·20	·49	35·5
14	227	3·21	·28	23·2
16·4	241	3·12	·23	21·0
18	248	3·15	·213	19·7
27	295	3·19	·145	15·6
37·5	338	3·18	·105	13·0

represent $(\alpha-\beta)/p$ and the abscissæ X/p. The points found experimentally were plotted on a large diagram and a continuous curve drawn through them in the ordinary manner. The values of $(\alpha-\beta)/p$ for certain values of X/p obtained from the curve are given in Table VI., and the degree of accuracy may be seen by comparing the results with the numbers given in Tables III., IV., and V.

10. The quantity γ may be found by equation (3) from measurements of the ratio n/n_0, n being the current at a distance x within the range where the currents have been found to be in agreement with equation (3). For this purpose the value of n may be taken at the distance x between the plates where the potential difference is 60 volts and $x\times p$ greater than ·3. The currents n_6 obtained at the distance 6 mm. with a force of 100 volts per cm. given in Table II. may therefore be used to calculate γ, n_2 being

equal to n_0 (except in the experiments with the pressures 3·32 and 2·30 mm. where n_2 differs by about 1 per cent. from n_0). It will be observed that the quantity $(\alpha-\beta)(S-x)$ which occurs in equation (3), may be written as the product $\left(\frac{\alpha-\beta}{p}\right)\left(1-\frac{60}{V}\right)\times pS$ where each factor has been found in terms of X/p, V, and $p\times S$ being given in terms of X/p, as

Fig. 5



X in volts per cm., p in mm. of mercury.

shown in Table II. The values of $(\alpha-\beta)/p$, V, $p\times S$, corresponding to the values of X/p given in Table II., are given in Table VI., also the values of n_6/n_0. The values of $1/\gamma=(\alpha-\beta)/\beta$ obtained by equation (3) are given in the last column of the table, n being the current at the distance x where the potential difference between the plates is 60 volts.

The numbers in the last column show that with a constant electric force X, the ratio $\alpha/\beta\,[=1+1/\gamma]$ increases with the

Table VI.

X/p.	V.	$p\times$S.	$\frac{\alpha-\beta}{p}$.	$\frac{n_\beta}{n_0}$.	$\frac{1}{\gamma}$.
13·6	325	24	·115	1·43	12·2
15·4	296	19·2	·145	1·48	12·1
18·1	264	14·6	·190	1·54	11·5
23·3	226	9·7	·275	1·64	10
30·0	207	6·9	·395	1·75	10·5
43·5	191	4·4	·63	1·80	10·2
62·1	186	3·0	·90	1·72	9·0
86	190	2·2	1·22	1·60	8·4
129	206	1·6	1·70	1·45	8·5
158	219	1·38	1·94	1·38	8·2
192	233	1·22	2·18	1·30	8·1

pressure. Near the point corresponding to the minimum sparking potential, X/p=62, β is approximately equal to α/10, thus the ratio β/α is much greater in neon than in other gases.

The values of α/p and β/p are given in Table VII., and α/p is represented in terms of X/p by the curve 2, fig. 5.

Table VII.

X/p.	$\frac{(\alpha-\beta)}{p}$	α/p.	β/p.
200	2·25	2·53	·28
160	1·95	2·19	·24
120	1·60	1·79	·19
100	1·40	1·57	·17
80	1·15	1·29	·14
60	·88	·99	·10
50	·72	·80	·076
40	·57	·63	·060
30	·39	·43	·038
25	·31	·34	·031
20	·220	·240	·020
15	·140	·152	·012
12·5	·100	·108	·008
10	·058	—	—
7·5	·030	—	—

11. In order to compare the photoelectric effect of radiation from the gas with the effect of ionization by the collisions of electrons with atoms of the gas, the current i from the cylinder C to the lower plate A (figs. 1 and 2) was measured while the current n was flowing from the upper to the lower plate. In these experiments the cylinder and the upper plate were at zero potential and the lower plate maintained at a positive potential.

It is difficult to estimate the proportion of the radiation from the gas that falls on the upper plate and on the cylinder. In neon the velocity of agitation of the electrons is large compared with the velocity in the direction of the electric forces, so that the current between the plates tends to spread out towards the edges, and this effect is of importance in considering the points in the gas from which the radiation originates. An approximate calculation shows that with the plates 6 mm. apart the amount of radiation falling on the upper plate is about the same as that falling on the cylinder.

The current from the lower plate to the cylinder was, in all cases, small compared with the current between the plates. The ratio $i/(n-n_0)$ increased with the distance between the plates, and when the distance was 6 mm. this ratio was about ·01 to ·015, depending on the pressure.

Hence the photoelectric effect due to radiation from the gas must be small compared with the increase in conductivity due to the process of ionization represented by the coefficients α and β.

In neon the rate of diffusion of electrons is large, and as the main current n tends to spread out towards the edges of the plates some of the positive ions may move along the lines of force from the lower plate to the cylinder. The current between the lower plate and the cylinder, due to radiation from the gas, may there be much less than one per cent. of the increase of the current $(n-n_0)$ between the plates.

The fact that there was a small current between the lower plate and the cylinder shows that with the larger distances between the plates the current n between the plates is slightly smaller than it would have been if plates of larger diameter had been used.

A corresponding effect was observed in finding the sparking potentials for different pressures and distances between the plates. For a given value of the product $p \times S$ the sparking potentials were the same within one volt with the plates 4, 5, or 6 mm. apart, but with larger

distances between the plates the sparking potential increased with the distance. With the plates 7 mm. apart the sparking potentials were two or three volts greater than those obtained with the smaller distances for the same values of the product $p \times S$. For this reason the sparking potentials used in these investigations were those obtained with the plates 5 mm. apart, as given in Table I.

12. The ratio α/X, as shown by the numbers given in Table VII., has a maximum value near the point where $X/p=60$, which is approximately the value of X/p for the minimum sparking potential. Thus for a given force X there is a certain pressure [X/60] at which ionization due to the collisions of electrons with atoms of the gas has a maximum effect.

The number of atoms ionized per centimetre by electrons moving in a uniform electric field is indicated by the formula $n=n_0\epsilon^{\alpha x}$ for the rate of increase of the number of electrons with the distances x. On an average each electron ionizes one atom of the gas in moving a distance x_1 in the direction of the force when $\epsilon^{\alpha x_1}=2$ or $\alpha x_1=\cdot 693$. Thus the potential required to double the current, $X \times x_1$ is $\cdot 693 \times X/\alpha$. The minimum value of this potential is near the point $X/p=60$ where $X \times x_1$ is 42·5 volts. At the point $X/p=30$ the potential $X_x x_1$ is 48·5, and at $X/p=120$. $X x_1$ is 46·2. The fact that $X \times x_1$ increases as the pressure is increased above the value corresponding to $X/p=60$ shows that the loss of energy of electrons in collisions with atoms that are not ionized increases. The number of atoms which can radiate energy is thus increased in comparison with the number that are ionized, and if the process of ionization represented by the coefficient β were due to radiation the ratio β/α should increase as the pressure is increased. This is contrary to the experimental results which show that β/α increases as the pressure is diminished. With a constant electric force X, the ratio α/X diminishes as the pressure is reduced below the value corresponding to $X/p=60$, and since the kinetic energy of the electrons increases as the pressure is reduced, the energy of the electrons in collisions with atoms that are ionized must increase. Thus as X/p increases the electrons acquire energy greater than the minimum amount required to ionize atoms of the gas.

Taking these points into consideration the results of the experiments may be examined more closely by the method that has already been described *. In another paper we

* Phil. Mag. vol. xiv. pp. 445 and 1071 (1923).

propose to continue the investigations on these lines and to compare the properties of neon and helium, when the experiments with helium are completed with the quartz apparatus.

13. The experiments are in agreement with the hypothesis that the process of ionization represented by the coefficient β is due to positive ions. It is impossible to decide from the determinations of the currents between parallel plates which of the two effects, that of ionizing atoms of the gas, or that of setting free electrons from the negative electrode, is the more important *. Huxley's experiments on discharges between coaxial cylinders show that with small values of X/p the principal effect of the positive ions is probably due to their actions in ionizing atoms of the gas †. The large values obtained for the coefficient β are in agreement with Huxley's experiments, which showed that the velocity of the positive ions increases rapidly with the electric force.

14. There are other points in connexion with these experiments which are of interest in considering the electrical properties of the atoms of the gas.

It cannot be supposed that the gas contained impurities in amounts that had an appreciable effect on the conductivity. The effects of small traces of impurities which get into the neon when it is kept in the apparatus increase continuously and are easily detected. When impurities are present in small amounts (which may not be observed spectroscopically), the effect on the conductivity is proportional to the amount of the impurity. For example, if a change of 2 volts were observed in the sparking potential after the gas had been 5 hours in the apparatus, a change of 4 volts was observed after 10 hours. Similar continuous changes are obtained in the values of the coefficients α and β. The fact that the impurities may be removed by two completely different methods which bring the gas to a state in which the same definite values of the sparking potential and of each of the coefficients α and β is obtained, shows that these coefficients are as characteristic of the pure gas as the lines of the spectrum.

In general it is difficult to determine the amount of an impurity required to produce a given change in the electrical properties of a monatomic gas.

With neon at a few millimetres pressure a very large

* 'Electricity in Gases,' pp. 330–332.

† H. G. L. Huxley, Phil. Mag. v. p. 721, April (1928).

change is produced with mercury vapour at 10^{-3} mm. pressure, and it is quite certain that gas with which the experiments were made did not contain mercury vapour at one hundredth of that pressure.

The large effect which impurities do produce in monatomic gases may be due to the fact that the velocity of agitation U of the electrons becomes very large in comparison with the velocity W in the direction of the electric force. In moving a distance x in the direction of the electric force the number of collisions an electron makes with molecules is Ux/Wl, where l is the mean free path between collisions with molecules. Thus the probability of collisions occurring with molecules which are present in small quantities increases with the ratio U/W, and a small number of molecules which are more easily ionized than atoms of a monatomic gas may have a large effect in increasing the conductivity.

15. The increase of conductivity due to ionization by collision is easily observed even when an electron collides with many atoms of the gas, as it moves in the direction of the electric force. With the gas at 44 mm. pressure, and the force 110 volts per centimetre, there is a 10 per cent. increase in the current when the distance between the plates is increased 2 mm. as shown by the figures in the last experiment recorded in Table IV.

The value of X/p in that experiment is about the same as in the luminous column of an electrodeless discharge in a tube 4 cm. in diameter with the neon at 1 mm. pressure. In this case the red lines of the spectrum are very intense, and the colour of the luminous column is a brilliant red.

The value of X/p in electrodeless discharges may be increased either by reducing the pressure of the gas or by reducing the diameter of the tube. Whichever method be adopted it is found that the colour of the discharge gradually changes from red to yellow. Hence the number of collisions which excite radiation in the red end of the spectrum diminishes in comparison with those which excite radiation of shorter wave-length, as X/p increases, or, as the kinetic energy of the electrons increases.

Thus with the smallest forces and largest pressures with which currents may be obtained, the energy of the electrons is not limited by critical properties of atoms to a value near the first resonance potential, which would prevent them acquiring energy in such amounts as are required to excite radiation in the visible spectrum or to ionize atoms of the gas.

Since the electrons acquire these amounts of energy when the ratio X/p is as small as 2·5, they must acquire energy in amounts much greater than that represented by the minimum ionizing potential when the pressure is reduced and X/p is increased to values of the order 10, or 20.

The experiments on the determination of the sparking potentials with the parallel plates show that the processes of ionization which maintain continuous currents sufficiently large to produce a luminous effect which is easily seen in the gas, are the same as those determined by the coefficients α and β in the experiments with small photoelectric currents. The small continuous currents of the order 10^{-7} ampere which are obtained with a battery of accumulators are maintained with the potential difference of $X \times S$ where S is the value of x for which the denominator of the fraction in equation 3 becomes infinite.

Thus the process of ionization represented by the coefficients α and β supply electrons at the rate which is required to maintain a continuous current of the order 10^{-7} ampere, and the collisions of the type which produce luminosity in these discharges must be supposed to occur also in the photoelectric currents*. Hence in all cases, however small the ratio X/p, the electrons acquire sufficient energy to ionize atoms of the gas and to cause atoms to radiate the long-waved light at the red end of the spectrum.

16. The sparking potentials have also been determined for helium with the improved form of apparatus in the quartz cylinder. As in neon, the sparking potentials were higher in the pure gas than in the gas with small traces of impurities, and the impurities are removed by the electrodeless discharge. The sparking potentials in pure helium are given in Table VIII. in terms of the product $p \times S$, the minimum potential being 223 volts near the point where $p \times S = 4$.

TABLE VIII.

$p \times S$	1·6	2	3	4	5	6	8	12	16
V.	360	280	230	223	225	232	249	287	324

V = sparking potentials in helium in volts.
S = distance between the plates in cm.
p = pressure of the gas in mm.

* 'Electricity in Gases,' p. 428.

These potentials are much higher than those found in earlier experiments. The method which was usually adopted to detect impurities, with a spectroscopic tube, is not sufficiently sensitive to indicate small traces of impurities which may have a considerable effect on the sparking potentials.

LXXXVII. *The Crystal Structure of* Cu_9Al_4. (*δ Copper–Aluminium.*) *By* Dr. A. J. Bradley *.

[Plate XV.]

THE alloy system Cu–Al has been investigated thermally and microscopically by several independent investigators. The most recent work is that of Stockdale †, who has also made a special study of the alloys rich in copper ‡. X-ray methods have been employed by several workers §, the most complete investigation by this method being that of Jette, Westgren, and Phragmèn ‖. The results obtained by the latter do not entirely agree with the equilibrium diagram proposed by Stockdale for alloys with between 16 and 39 per cent. of aluminium. We have recently made an examination of some alloys in this range, which confirms neither of the above results, but corroborates the results of further work, done recently by Westgren and Phragmèn, and communicated privately to us.

The most important point settled by this recent investigation is that Stockdale's δ-phase actually only extends over the range between 16 and 19 per cent. of aluminium. Beyond 19 per cent. of aluminium the photograms become rather difficult to interpret, and it was evident that the most satisfactory way to tackle the problem was to start by determining the way the atoms were arranged in the δ-phase, with between 16 per cent. and 19 per cent. of aluminium.

The clue to the crystal structure of the δ-phase is given by the close resemblance between the photograms of this phase and those obtained from alloys of copper and zinc containing between 61 and 69 per cent. of zinc. The structure of the

* Communicated by Prof. W. L. Bragg, F.R.S.

† Journ. Inst. Metals, xxxi. p. 275 (1924).

‡ Journ. Inst. Metals, xxviii. p. 273 (1922).

§ Owen & Preston, Proc. Phys. Soc. Lond. xxxvi. p. 14 (1923); Jette, Westgren, & Phragmèn, Journ. Inst. Metals, xxxi. p. 193 (1924).

‖ *Loc. cit.*

latter alloys was found by Bradley and Thewlis *, and in the present paper an attempt has been made to trace out the relationship between the two structures.

Data.

Jette, Westgren, and Phragmèn (*loc. cit.*) obtained single crystals of alloys with 16 per cent. of aluminium, large enough to use for a Laue photograph. This showed that the crystal symmetry was cubic, the class being T^d, O, or O^h.

We have taken powder photograms of various alloys within the range 16–19 per cent. aluminium, and find that all the lines fit in with the assumption that the structure is cubic. The results obtained from two photograms are given below, in Table I. Copies of these photograms are shown in Pl. XV. together with a film of copper-zinc taken

TABLE I.

		Alloy A.			Alloy B.		
Σh^2.	Radiation.	$\sin^2\theta$ Obs.	$\sin^2\theta$ Calc.	Intensity.	$\sin^2\theta$ Obs.	$\sin^2\theta$ Calc.	Intensity.
5	$K\alpha$	·039	·039	m.–w.	·039	·039	m.–w.
6	$K\alpha$	·047	·047	m.	·047	·047	m.
9	$K\alpha$	·071	·071	m.	·070	·070	m.
12	$K\alpha$	·095	·094	w.	·093	·094	w.
14	$K\alpha$	·111	·110	w.	·109	·109	w.
18	$K\alpha$	·141	·141	v.v.st.	·140	·141	v.v.st.
22	$K\alpha$	·174	·172	m.	·172	·172	m.
24	$K\alpha$	·189	·189	m.	·187	·188	m.
26	$K\alpha$	·205	·204	w.	·202	·203	w.
27	$K\alpha$	·213	·212	w.	·211	·211	w.
29	$K\alpha$	·228	·227	v.w.	·227	·227	v.w.
33	$K\alpha$	·260	·259	v.w.	·259	·258	v.w.
36	$K\alpha$	·284	·282	v.st.	·281	·281	v.st.
38	$K\alpha$	·299	·298	w.	·298	·297	w.
41	$K\alpha$	·323	·321	v.w.	·320	·320	v.w.
42	$K\alpha$	·331	·329	v.w.	·329	·328	v.w.
46	$K\alpha$	·362	·360	m.	·360	·360	w.
48	$K\alpha$	·378	·376	m.	·375	·375	m.
50	$K\alpha$	·393	·392	m.	·391	·391	w.
52	$K\alpha$	·408	·407	v.w.			
54	$K\alpha$	·424	·423	v.st.	·422	·422	v.st.
56	$K\alpha$	·441	·439	w.			
62	$K\alpha$	·487	·486	v.w.			
66	$K\alpha$	·518	·517	st.	·515	·516	st.

* Proc. Roy. Soc. A, cxii. p. 678 (1926).

TABLE I. (*cont.*).

		Alloy A.			Alloy B.		
Σh^2.	Radiation.	$\sin^2\theta$ Obs.	$\sin^2\theta$ Calc.	Intensity.	$\sin^2\theta$ Obs.	$\sin^2\theta$ Calc.	Intensity.
68	$K\alpha$	·534	·533	w.	·531	·531	w.
70	$K\alpha$	·550	·548	v.w.	·546	·547	v.w.
72	$K\alpha$	·566	·564	st.	·562	·563	m.
74	$K\alpha$	·581	·580	v.w.	·578	·578	v.w.
76	$K\alpha$	·596	·595	w.	·594	·594	v.w.
78	$K\alpha$	·612	·611	w.	·609	·610	v.w.
81	$K\alpha$	·634	·635	v.w.			
82	$K\alpha$	·642	·642	v.w.			
90	$K\alpha_1$	·704	·704	m.	·704	·703	m.
	$K\alpha_2$	·708	·707	m.			
98	$K\alpha_1$	·767	·767	m.	·764	·764	m.
	$K\alpha_2$	·771	·770	m.	·765	·765	m.
102	$K\alpha_1$	·798	·798	m.	·795	·795	m.
	$K\alpha_2$	·802	·802	m.	·800	·800	m.
104	$K\alpha_1$	·814	·813	v.w.			
	$K\alpha_2$	·818	·818	v.w.			
106	$K\alpha_1$	·829	·829	v.w.			
	$K\alpha_2$	·833	·833	v.w.			
108	$K\alpha_1$	·845	·845	m.	·842	·842	m.
	$K\alpha_2$	·849	·849	m.	·846	·847	m.
110	$K\alpha_1$	·860	·860	v.w.			
	$K\alpha_2$	·865	·865	v.w.			
114	$K\alpha_1$	·892	·892	st.	·889	·889	st.
	$K\alpha_2$	·896	·896	st.	·894	·894	m.
117	$K\alpha_1$	·915	·915	v.w.			
	$K\alpha_2$	·920	·920	v.w.			
118	$K\alpha_1$	·923	·923	w.			
	$K\alpha_2$	·927	·928	w.			
120	$K\alpha_1$	·938	·938	st.	·936	·936	st.
	$K\alpha_2$	·943	·943	m.	·941	·941	m.
122	$K\alpha_1$	·954	·954	m.			
	$K\alpha_2$	·959	·959	w.			

for comparison. In each case the radiation employed was obtained from a hot cathode tube with a copper anticathode, the β-radiation being cut off by the use of a nickel screen. Only one β-line can be observed on each film, corresponding to the strongest α-line. At the ends of the photograms the α-doublet is clearly resolved. Only measurements from lines which are resolved have been used for the determination of the lattice dimensions. By this means it has been possible to get a high degree of accuracy in these calculations.

The number of atoms per unit cell was found to be the same in the copper-aluminium structure as in the copper-zinc structure, namely, 52. The data from which this figure was obtained are given in Table II.

TABLE II.

Radiation.	$\frac{\sin^2\theta}{\Sigma h^2}$.	Length of Unit Cell.	Density.	Per cent. Al.	Mean At. Wt.	Atoms per Unit Cell.
α_1	·007821	8·691	6·74	17·85	51·26	52·3
α_2	·007860	8·691				
α_1	·007799	8·704	6·64	18·66	50·81	52·2
α_2	·007741	8·703				

The values of $\frac{\sin^2\theta}{\Sigma h^2}$, shown above, are the mean of all values from the lines where the α-doublet is resolved.

Derivation of the Structure of δ Cu–Al *from the* γ Cu–Zn *Type.*

The similarity between the copper-aluminium and copper-zinc photograms, which has been pointed out by Westgren and Phragmèn, is so great that there can be no doubt that the structures are very closely related. The differences are, however, sufficiently marked to show that the structures are not quite the same in every respect. By carefully studying the difference it has been found possible to assign a structure to δ Cu–Al by a slight modification of the copper-zinc structure. The structure so obtained has the requisite symmetry shown by the Laue photograph. Starting out from the assumption that the structure of δ Cu–Al is based on the γ Cu–Zn type of structure, a variety of possible modifications suggest themselves. A choice between these possibilities has been made, taking the intensities of the lines as the sole guide for this purpose. The validity of the structure ultimately found rests on the excellent way in which it explains the observed intensities, including the differences in intensity of corresponding lines on the copper-aluminium and the copper-zinc photograms.

The 52 atoms in the unit cube of the copper-zinc type of structure are divided among four groups of structurally equivalent atoms, which may be called A, B, C, and D atoms

respectively. There are eight A atoms, eight B atoms, twelve C atoms, and twenty-four D atoms. The A and D atoms are zinc, the B and C atoms are copper, so that that there are 32 zinc atoms and 20 copper atoms. The relative proportions of the two constituents in the copper-aluminium alloy is quite different, there being about twice as many copper atoms as aluminium atoms. The distribution of the atoms in δ Cu–Al must therefore be quite different from that in the γ Cu–Zn alloy.

This fact gives a possible explanation of the differences in the intensities in the photograms of the two alloys. The photograms differ in two ways. The relative intensities of the lines on the γ Cu–Zn photogram are not in every case the same as those of corresponding lines on the δ Cu–Al photograms. There are, moreover, some additional lines on the Cu–Al photograms which, for the most part, belong to planes with $h+k+l$ odd, indicating that the unit cube is primitive and not body-centred, as in the case of γ-brass.

These intensity changes cannot be accounted for by supposing that the *positions* of the atoms have suffered a slight *displacement*, the effect of which would be to produce a slight change in the least deviated reflexions and a much larger change in the most deviated reflexions. This is just the reverse of what one observes. It is therefore safe to conclude that the atoms, as a whole, occupy almost identical positions in the two alloys. The intensity changes must be ascribed to the differences in the distribution of atoms of the two species, and they can therefore be utilized in order to find how the copper and aluminium atoms are distributed.

The first condition imposed by the reflexions is that the unit cube of δ Cu–Al must be primitive. In order to see how this change from the γ Cu–Zn type can be brought about, it is only necessary to consider what arrangement is responsible for the γ Cu–Zn structure being body-centred. The γ Cu–Zn structure is body-centred because there is for every atom with coordinates $x\ y\ z$, a corresponding atom with coordinates $x+\frac{1}{2}\ y+\frac{1}{2}\ z+\frac{1}{2}$, and each of these pairs of atoms is of the same kind. If they were of different kinds the unit would be primitive. Thus the unit cube of the Cu–Al structure will be primitive, provided that, in at least one of the four groups of atoms, an atom with coordinates $x\ y\ z$ is aluminium and an atom with coordinates $x+\frac{1}{2}\ y+\frac{1}{2}\ z+\frac{1}{2}$ is copper. In other words, each group of atoms, A, B, C, D, may itself consist of two structurally independent sets of atoms. There are, therefore, eight possible independent sets of atoms in the δ Cu–Al structure.

Assuming that the coordinates of the atoms in the copper-aluminium structure are the same as those in the copper-zinc structure, the 52 atoms of the δ Cu–Al structure can be divided into eight sets of atoms with the coordinates shown in Table III. This division of the atoms is the only one consistent with the observed symmetry, and no other arrangement based on the γ Cu–Zn type is possible for δ Cu–Al.

From Table III. it is seen that the 52 atoms of the unit cube of Cu–Al may be divided into 4 A_1 atoms, 4 A_2 atoms, 4 B_1 atoms, 4 B_2 atoms, 6 C_1 atoms, 6 C_2 atoms, 12 D_1 atoms, and 12 D_2 atoms. A detailed examination of the differences

TABLE III.

The Coordinates of the Atoms in δ Cu–Al.

A *atoms.*

Subgroup 1.

$(a\ a\ a)$, $(a\ -a\ -a)$, $(-a\ a\ -a)$, $(-a\ -a\ a)$.

Subgroup 2.

$(\frac{1}{2}+a\ \frac{1}{2}+a\ \frac{1}{2}+a)$, $(\frac{1}{2}+a\ \frac{1}{2}-a\ \frac{1}{2}-a)$, $(\frac{1}{2}-a\ \frac{1}{2}+a\ \frac{1}{2}-a)$, $(\frac{1}{2}-a\ \frac{1}{2}-a\ \frac{1}{2}+a)$.

B *atoms.*

Subgroup 1.

$(-b\ -b\ -b)$, $(-b\ b\ b)$, $(b\ -b\ b)$, $(b\ b\ -b)$.

Subgroup 2.

$(\frac{1}{2}-b\ \frac{1}{2}-b\ \frac{1}{2}-b)$, $(\frac{1}{2}-b\ \frac{1}{2}+b\ \frac{1}{2}+b)$, $(\frac{1}{2}+b\ \frac{1}{2}-b\ \frac{1}{2}+b)$, $(\frac{1}{2}+b\ \frac{1}{2}+b\ \frac{1}{2}-b)$.

C *atoms.*

Subgroup 1.

$(c\ 0\ 0)$, $(-c\ 0\ 0)$, $(0\ c\ 0)$, $(0\ -c\ 0)$, $(0\ 0\ c)$, $(0\ 0\ -c)$.

Subgroup 2.

$(\frac{1}{2}+c\ 0\ 0)$, $(\frac{1}{2}-c\ 0\ 0)$, $(0\ \frac{1}{2}+c\ 0)$, $(0\ \frac{1}{2}-c\ 0)$, $(0\ 0\ \frac{1}{2}+c)$, $(0\ 0\ \frac{1}{2}-c)$.

D *atoms.*

Subgroup 1.

$(d\ d\ e)$, $(d\ -d\ -e)$, $(-d\ d\ -e)$, $(-d\ -d\ e)$.
$(d\ e\ d)$, $(d\ -e\ -d)$, $(-d\ e\ -d)$, $(-d\ -e\ d)$.
$(e\ d\ d)$, $(e\ -d\ -d)$, $(-e\ d\ -d)$, $(-e\ -d\ d)$.

Subgroup 2.

$(\frac{1}{2}+d\ \frac{1}{2}+d\ \frac{1}{2}+e)$, $(\frac{1}{2}+d\ \frac{1}{2}-d\ \frac{1}{2}-e)$, $(\frac{1}{2}-d\ \frac{1}{2}+d\ \frac{1}{2}-e)$, $(\frac{1}{2}-d\ \frac{1}{2}-d\ \frac{1}{2}+e)$.
$(\frac{1}{2}+d\ \frac{1}{2}+e\ \frac{1}{2}+d)$, $(\frac{1}{2}+d\ \frac{1}{2}-e\ \frac{1}{2}-d)$, $(\frac{1}{2}-d\ \frac{1}{2}+e\ \frac{1}{2}-d)$, $(\frac{1}{2}-d\ \frac{1}{2}-e\ \frac{1}{2}+d)$.
$(\frac{1}{2}+e\ \frac{1}{2}+d\ \frac{1}{2}+d)$, $(\frac{1}{2}+e\ \frac{1}{2}-d\ \frac{1}{2}-d)$, $(\frac{1}{2}-e\ \frac{1}{2}+d\ \frac{1}{2}-d)$, $(\frac{1}{2}-e\ \frac{1}{2}-d\ \frac{1}{2}+d)$.

$a=0{\cdot}10_0$, $b=0{\cdot}16_7$, $c=0{\cdot}35_5$, $d=0{\cdot}30_5$, $e=0{\cdot}04_5$.

between the Cu–Al and the Cu–Zn photograms enables us to find out which of these atoms are copper and which are aluminium.

There are nine different ways in which the atoms may be distributed with approximately the given proportions of copper and aluminium atoms. These are tabulated below.

Table IV.

Possible Ways of placing the Aluminium Atoms in δ Cu–Al.

(*a*) With 15·9 per cent. aluminium.

(1) $4\,A_1$, $4\,A_2$, $4\,B_1$, $4\,B_2$.
(2) $12\,D_1$, $4\,A_1$.
(3) $12\,D_1$, $4\,A_2$.
(4) $12\,D_1$, $4\,B_1$.
(5) $12\,D_1$. $4\,B_2$.
(6) $6\,C_1$, $6\,C_2$, $4\,A_1$.
(7) $6\,C_1$, $6\,C_2$, $4\,B_1$.

(*b*) With 18·4 per cent. aluminium.

(8) $12\,D_1$, $6\,C_1$.
(9) $12\,D_1$, $6\,C_2$.

A detailed examination of the nine possible solutions is given below, in which it is shown that arrangement (3) is the only possible solution.

Method of Elimination.

The possible solutions based on the γ Cu–Zn type of structure fall into three classes, according to the degree in which they fit in with the observations. In the first place, solution (1) can be ruled out without any detailed consideration, since it is a body-centred arrangement, which would give no reflexions from planes with $h+k+l$ odd. The remainder require fuller treatment, but, with the exception of (3) and (4), only reflexions from planes with $h+k+l$ odd need be considered in order to show that these solutions must be rejected. This greatly shortens the arithmetical work and only leaves (3) and (4) for a final detailed treatment.

Table V. gives the calculated values of $\frac{NS^2}{\Sigma h^2}$ for a number of planes with low indices with $h+k+l$ odd. For these calculations we have taken the scattering power of each atom to be proportional to its atomic number, so that if Cu + Al = 1, Cu–Al = 0·38, and 2 Cu = 1·38.

The structure amplitudes for planes with $h+k+l$ odd are as follows :—

A atoms,

$$S_{--} = (4\cos ha\cos ka\cos la - 4i\sin ha\sin ka\sin la)(X_A - Y_A).$$

B atoms,

$$S = (4\cos hb\cos kb\cos lb + 4i\sin hb\sin kb\sin lb)(X_B - Y_B).$$

C atoms,

$$S = (2\cos hc + 2\cos kc + 2\cos lc)(X_C - Y_C).$$

D atoms,

$$S = (4\cos hd\cos kd\cos le - 4i\sin hd\sin kd\sin le + 4\cos hd\cos ke\cos ld - 4i\sin hd\sin ke\sin ld + 4\cos he\cos kd\cos ld - 4i\sin he\sin kd\sin ld)(X_D - Y_D).$$

X and Y are numbers proportional to the scattering powers of the atoms in the respective sub-groups. Hence, if atoms in corresponding sub-groups (*e. g.* both A_1 atoms and A_2 atoms) are of the same kind, they contribute nothing to the value of S, but if the first set were copper and the second set aluminium, there might be a difference effect giving rise to a reflexion.

Table V.

Σh^2.	Observed Intensity.	$\frac{NS^2}{\Sigma h^2}$								
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
3	..... —	—	10	2	2	12	2	3	8	13
5	..... m.	—	3	10	11	3	1	1	5	8
9	..... m.	—	12	23	19	21	2	4	39	4
11	..... —	—	5	—	2	5	1	—	3	1
13	..... —	—	1	0	—	4	—	1	1	7
17	..... —	—	2	1	2	—	2	—	—	—
19	..... —	—	—	4	3	1	1	1	4	1
21	..... —	—	4	1	2	6	1	2	8	1
25	..... —	—	4	—	4	3	1	1	1	3
27	..... w.	—	4	7	6	3	1	2	8	5
29	..... v.w.	—	—	4	2	1	1	—	1	2
33	..... v.w.	—	11	10	9	14	1	1	12	13
35	..... —	—	7	2	7	3	—	—	2	4

Table V. shows clearly that only solutions (3) and (4) are possible. In order to decide between these two possibilities,

we require to consider the intensities of planes for which $h+k+l$ is even. In these cases S is given by the same formula as above, but X − Y is replaced by X + Y. Table VI. gives the calculated values of $\frac{NS^2}{\Sigma h^2}$, for the two possible solutions. In each case the value of line 18, the strongest line on the film, is put as 100. It seems that column 5 is in somewhat better agreement with the observed intensities than column 6, so that solution (3) is indicated as the true structure.

No attempt has been made to get a more accurate evaluation of the parameters, because the good agreement already obtained between the observed and calculated values indicates that the parameters of the copper-zinc structure are very closely adhered to, and with eight parameters to fix, a more accurate evaluation would be very difficult.

The observed and calculated values of the copper-zinc intensities are given in Table VI. for comparison with the values for copper-aluminium. This table may be compared with the copies of the photograms. It is evident that the differences in the distribution of the atoms in the two alloys completely account for the differences in the photograms.

Description of the Structure.

The structure of δ copper-aluminium containing 16–19 per cent. of aluminium is cubic, with 52 atoms per unit cell. These atoms have almost the same positions as the 52 atoms in the copper-zinc structure, containing 61–69 per cent. zinc. There are 16 aluminium atoms and 36 copper atoms in the "ideal" alloy, so that it may be represented by the stoichiometric formula Cu_9Al_4, corresponding to a composition with 15·9 per cent. of aluminium. In alloys containing a slight excess of aluminium, aluminium atoms appear to replace copper atoms in a haphazard fashion, so that there is no appreciable difference in character between a 16 per cent. alloy and a 19 per cent. alloy.

The coordinates of the atoms are given in Table III. The copper atoms consist of 4 A_1, 4 B_1, 4 B_2, 6 C_1, 6 C_2, and 12 D_2 atoms. The aluminium atoms consist of 4 A_2 atoms and 12 D_1 atoms. The structure can be best understood if the two subgroups of atoms (*e. g.* the A_1 and the A_2 subgroups) are considered separately. Each subgroup of atoms containing atoms A_1, B_1, C_1, and D_1, forms part of a cluster of 26 atoms grouped around the centre of the unit cell. A similar cluster of 26 atoms, such as A_2, is grouped about the

TABLE VI.

	Cu_5Zn_8.		Cu_9Al_4.		
Σh^2.	Observed Intensity.	$\frac{NS^2}{\Sigma h^2}$.	Observed Intensity.	$\frac{NS^2}{\Sigma h^2}$.	$\frac{NS^2}{\Sigma h^2}$.
				Case 3.	Case 4.
(1)	(2)	(3)	(4)	(5)	(6)
3	—	—	—	0·4	0·4
4	—	0	—	0·1	0·9
5	—	—	w.–m.	1·9	2·3
6	—	0·6	m.	3·9	1·1
8	—	0·1	—	0·1	0·0
9	—	—	m.	4·3	3·9
10	—	0·2	—	0·3	0·6
11	—	—	—	0·1	0·3
12	m.	5·0	w.	2·2	2·5
13	—	—	—	0·0	0·3
14	m.	3·9	w.	1·8	3·3
16	—	0	—	0·0	0·1
17	—	—	—	0·2	0·5
18	v.v.st.	100	v.v.st.	100	100
19	—	—	—	0·7	0·6
20	v.w.	0·7	—	0·3	0·9
21	—	—	—	0·1	0·3
22	m.–st.	9·7	m.	6·9	11·5
24	m.	5·8	m.	7·2	7·2
25	—	—	—	0·0	0·7
26	m.	4·1	w.	1·9	5·4
27	—	—	w.	1·3	1·2
29	—	—	v.w.	0·7	0·4
30	w.	1·3	—	0·5	0·3
31	—	0·8	—	0·5	0·9
33	—	—	v.w.	1·8	1·8
34	—	1·0	—	0·2	0·6
35	—	—	—	0·4	1·4
36	st.–m.	9·7	v.st.	12·7	10·3

corners of the unit cell. Thus we have around the centre of the unit cube 14 copper atoms and 12 aluminium atoms, and around the corners of the unit cell 22 copper atoms and 4 aluminium atoms.

The essential difference between the δ Cu–Al structure and the γ Cu–Zn structure is that in the latter case the cluster of atoms at the centre of the unit is the same as that at the corners of the unit cell. In this way the structure of Cu_5Zn_8 is analogous to a body-centred cube, whereas that of Cu_9Al_4 is analogous to the CsCl type of structure. This relation between the two structures is shown in Table VII.

Table VII.

Alloy.	Atoms in Centre Cluster.	Atoms in Corner Cluster.
Cu_5Zn_8	Cu—4 B, 6 C. Zn—4 A, 12 D.	Cu—4 B, 6 C. Zn—4 A, 12 D.
Cu_9Al_4	Cu—4 B, 6 C, 12 D. Al—4 A.	Cu—4 A, 4 B, 6 C. Al—12 D.

The structure of Cu_9Al_4 has the symmetry of the T^d class like that of Cu_5Zn_8, but the space-group is not the same, being T_1^d in the former alloy, and T_3^d in the latter case.

Summary.

(1) Powder photograms of δ copper-aluminium containing 16–19 per cent. aluminium show a cubic structure with 52 atoms per unit cell.

(2) The space-group is T_1^d, and there are eight sets of structurally equivalent atoms.

(3) There are 36 copper atoms and 16 aluminium atoms in each unit cube, corresponding to the formula Cu_9Al_4.

(4) The structure is essentially of the CsCl type, each lattice point being replaced by a cluster of 26 atoms, with tetrahedral symmetry. The cluster around the centre of the unit cell contains a different number of aluminium atoms from that around the corners of the unit cell.

(5) The coordinates of the atoms are not appreciably different from those in the alloy Cu_5Zn_8.

The author is indebted to Prof. W. L. Bragg, F.R.S., for his kind interest in this work, and to the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship, enabling the work to be carried out.

LXXXVIII. *The Energy Losses of Electrons in Hydrogen.* *By* H. Jones, *B.Sc.*,* *and* R. Whiddington, *M.A*, *D.Sc.*, *F.R.S.*, *Cavendish Professor of Physics, The University of Leeds* †.

Introduction.

THE energy lost by an electron of determined velocity, suffering effective collision with a normal hydrogen molecule, is not to be deduced with any precision from the results of electron impact experiments which have hitherto been made‡. Since the ultra-violet spectrum of H_2 has been successfully analysed the energy levels of the molecule are known with accuracy, and it becomes interesting to examine the relation between these and the energy lost by electrons of various known velocities, and also the frequency with which certain excitation processes occur.

In essence the experimental method adopted consists in the passing of a beam of electrons through the gas under investigation and analysing the resulting stream by means of a magnetic spectrum device. As might be anticipated the issuing beam contains groups of definite energy, the determination of the energy differences between these groups and the relative number of electrons in each being the object of the experiment. No attempt was made to investigate the electron streams scattered in different directions. Only those electrons flung off in approximately their original direction are examined in these experiments, those scattered in different directions being made the subject of a separate investigation now in progress.

Apparatus.

The essentials of the apparatus are indicated in the accompanying diagram (fig. 1). Electrons from the filament F are accelerated towards the grid G by a suitable electric field and traverse the collision space included between G_1 and a second grid G_2; thereafter the composite beam is accelerated again by a second suitable electric field between G_2 and a slit system S_1S_2, after which the fine beam so produced is deflected in a uniform magnetic field before affecting the

* Communicated by the Authors.

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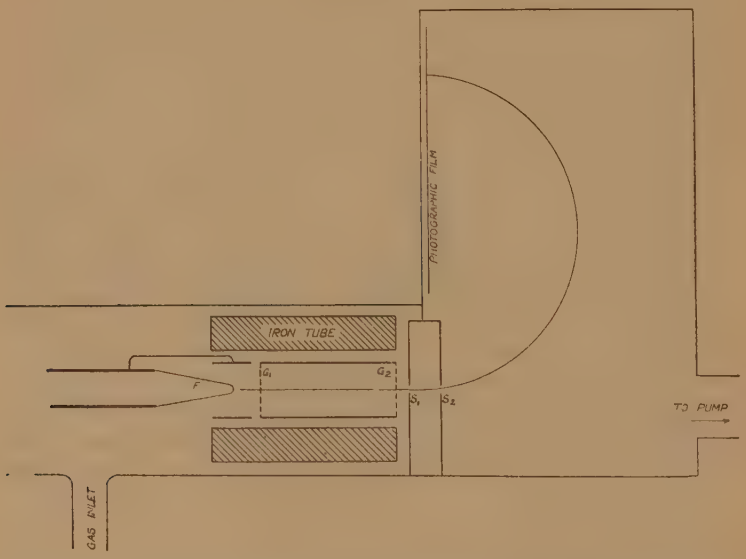
‡ Franck and Jordan, 'Anregung von Quanten Sprüngen durch Stösse,' p. 256.

photographic film. Since in operation the pressure in the collision space was usually about 10^{-2} mm. Hg., whilst in the camera it had to be kept at not more than 10^{-4}, a fast working pump system was chosen, viz., a Kaye Backhurst steel diffusion pump backed with a Pfeiffer rotary oil pump. This combination is very satisfactory for rapid evacuation.

The magnetic field across the camera was produced by two large coils measuring 31·5 cm. long, 23 cm. high, 15·5 cm. wide, separated by a distance of 9 cm. Calibration in the usual manner showed the field to be 22·0 gauss per ampere, and to be sufficiently uniform over a considerable region at

Fig. 1.



the centre. On account of the comparatively high values of the field employed (13 gauss) and the circumstance that the apparatus pointed north and south, it was not considered necessary to compensate for the earth's field.

The hydrogen was admitted to the all-glass apparatus through the gas-inlet shown in fig. 1, and every care was taken to ensure the purity of the gas supplied, which, electrolysed from barium hydroxide in a eudiometer, passed *via* an all-metal needle valve through the collision space G_1G_2.

It was found convenient to have, in this part of the apparatus, the usual pentoxide tube drying arrangements,

the hydrogen being stored in a large glass reservoir at a pressure of a few centimetres of mercury, a liquid air-trap of ample dimensions intervening immediately before the above-mentioned gas inlet.

A Pirani gauge found a place on this side of the apparatus and proved to be particularly convenient for adjusting the pressure balance at any desired value, calibrated by reference to a permanently connected McLeod gauge. The Pirani readings were usually regarded as sufficient, but for the determination of the probability of excitation at high voltages, where a very accurate knowledge of the pressure is of first importance, a reading was taken directly on the McLeod gauge for each photograph.

To obtain enough photographic effect with electrons of velocity below, say, 200 volts, it is necessary to use some form of suitably sensitized films. Eastman duplitized X-ray films washed in a solution of vaseline in ether—of suitable strength—were employed *. By sensitizing large sheets and cutting off the films for use across the direction in which the sheet had been dipped, it was possible to obtain films along whose length the grease was of approximately uniform density. The necessity for the application of grease (or any fluorescent substance) must always make the comparison of intensities of widely different parts of the film somewhat uncertain. In the present experiments only portions of a few millimetres in extent were ever considered.

The Cathode and Slit System.

The principal problem in technique was that of obtaining a well-directed electron beam passing through a distance of some 3 cm. in the gas, then entering the camera, across which a uniform, or very nearly uniform, magnetic field must exist.

Two general possibilities are obvious. One may, or may not, use a compensating device over the collision space. Both methods have been tried. In the first case when no compensation is applied the electron stream in the gas follows its natural circular path of radius appropriate to the potential and magnetic field. The cathode for this purpose is introduced through a side tube inclined at about 50° to the base of the camera. For initial velocities greater than, say, 50 volts, this arrangement was fairly satisfactory for obtaining energy differences, but was not suitable for low

* G. F. Brett, Proc. Leeds Phil. & Lit. Soc. 1925.

velocities or for intensity measurements, and was not, therefore, our final choice.

Compensation may be effected by coils or by an iron cylinder suitably placed. A number of trials of both schemes led to the final adoption of a cylindrical iron shield placed in the manner shown in fig. 1.

The presence of so much iron produces a rather serious lack of uniformity in the field across the camera, a difficulty met by sacrificing the main advantage of focussing (shortness of exposure) by using two narrow slits. The first slit was 2 mm. long and 0·025 mm. wide, the second was 8 mm. long and 0·5 mm. wide, separated by a distance of 5 mm., the second being in the same plane as the photographic film, whilst the line joining the two slits was accurately at right angles to this plane. Care was taken to see that the two slits were parallel and that their direction was that of the magnetic field. In this way—since the field between the two slits is reduced by the presence of the iron—electrons which are moving perpendicular to the face of the first slit enter the camera and strike the photographic film normally. This arrangement was found to give lines of considerable sharpness.

The filaments which have been used throughout were of pure tungsten wire designed to carry a current of 0·2 ampere. They were in general 3 mm. long and were bent in hairpin form, bringing the central portion close to the grid G_1.

The total fall of potential down the filament and leads under working conditions, *i. e.*, at the temperature generally used, was 1·24 volts, but on account of the "end effect" it could be seen that only the middle portion glowed at all vigorously. In addition, the grid—a closely-wound flat tungsten spiral—was placed at a distance of not more than 1 mm. from the centre of the filament. Consequently, the fall of potential down the effective portion could not have been more than 0·2 or 0·3 volt.

The copper cylinder surrounding the filament and connected to the negative end serves to prevent electrons passing directly to the iron cylinder. An advantage of using very small filaments consuming little energy is that exposures can be extended to any length without appreciable heating up of the apparatus. An equally important advantage is that dissociation as a result of contact with the glowing tungsten is reduced to an almost negligible amount.

When the velocity of the electrons entering the camera is below about 25 volts the photographic effect, even

with sensitized films, becomes very weak. In addition to which, external disturbances, *e.g.*, the earth's field, become relatively much more effective. This limitation has been overcome in these experiments by applying a permanent accelerating potential of 75 volts between the grid G_2 at the end of the iron cylinder and the face of the first slit of the camera. It is essential that the grid and the slit face—which are separated by about 1 mm.—shall be parallel, otherwise the electrons entering the first slit will not be moving in such a direction as to pass through the second. This, of course, applies only when the velocity of the electrons passing through the second grid is small, say one or two volts. When it is greater than this there will always be a certain number of those scattered in the collision space able to enter the camera, even when the grid and slit face are not quite parallel.

To obtain photographs giving information about the excitation probability in the neighbourhood of the critical potential requires that electrons, which after suffering effective collision, thus having velocities of one or two volts, shall in general pass a distance of one or two cm. inside the iron cylinder. The dimensions of this cylinder were such that an electron of 1-volt velocity moving within it with the external magnetic field 13·2 gauss followed a path of radius greater than 40 cm. From this it will be seen that the shielding is sufficiently complete for the present purpose. This is borne out by the photographs obtained at low voltages.

The thermionic current was measured with a Weston galvanometer of sensitivity 29×10^{-5} ampere per division. A 2-volt lamp was placed in the high-tension circuit to act as a fuse. As a rule arcing did not occur with the filament and grid separated by not more than 1 mm. unless the pressure was raised beyond 0·01 mm. Hg.

It is essential after introducing a film into the camera to continue the evacuation for not less than an hour and a half. This was necessary on account of moisture and any vapours given off by the film arising from the application of grease. After this time a reading of the McLeod gauge in general showed the pressure to be less than 10^{-4} mm. Hg., at which pressure the magnetic spectrum was found to consist of one sharp line only. There was no difficulty experienced by adjustment of the needle valve in obtaining a pressure balance of gas very close to the desired value, and in this state the apparatus was allowed to stand for five or ten minutes; the reading of the Pirani would then be taken and

the exposure made. With the small filaments used no sensible change in the pressure could be observed during exposures lasting up to fifteen minutes.

The question of the purity of the hydrogen is clearly of such importance that, although the greatest care was taken to exclude impurities, it was nevertheless thought advisable to obtain check photographs with air and oxygen*. These photographs obtained with high electron velocities were, even to a casual inspection, quite unlike those obtained with pure hydrogen under similar conditions when a single well-defined line is obtained. At velocities below 20 volts, the photographs with H_2 indicate the frequent occurrence of an additional energy loss of a smaller amount. The very characteristic dependence of the intensity of the line corresponding to this lower loss on the velocity of the impacting electrons, particularly the fact that the line completely vanishes for high velocities, removes any doubt concerning its origin.

Related to the question of impurities is that of the relative number of atoms and molecules at any instant in the collision space. As pointed out by Franck and Jordan†, the conditions favouring a maximum percentage of molecules are: (1) low pressures, (2) the use of suitable metal surfaces, (3) low temperatures, (4) extreme purity of the gas, (5) the removal of gas layers from the walls of the collision space. In the present experiments the first four points were fairly well complied with, but the last condition was not, since it did not appear practical to bake out the metal parts before each exposure. Favouring a large percentage of molecules was the circumstance that a continuous stream of gas was being passed through the collision space. It is to be expected then that the energy losses shown in the photographs are related to the molecular, not the atomic, levels. With hydrogen, as the numerical results will show, this is the case.

Calculation of Data from Photographs.

As already pointed out, the photographs of the magnetic spectrum with gas present, of which just a single illustrative

* The figures give the energy losses of the primary electrons in volts, and the remarks refer to the corresponding lines on the photographs.

Oxygen .. 16·1 (weak), 13·0 (strong), 10·8 (weak), 8·1 (strong).

Air ..... 13·6 (very strong), 8·6 (very strong).

These results are only approximate, the lines on the air photograph being probably combinations of lines due to both oxygen and nitrogen lying in this neighbourhood.

† Franck and Jordan, *loc. cit.* p. 259.

example is reproduced here (fig. 2), usually consist of several separated lines or bands, the least deviated line corresponding to the full velocity electrons which may have come directly from the filament or more usually by way of one or more elastic reflexions. It is convenient to express any other lower velocity line in terms of the energy difference in volts between it and the full velocity line.

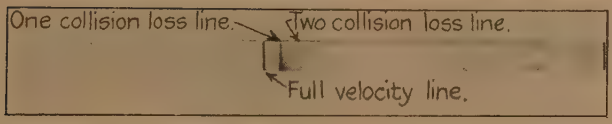
In the initial experiments when the focussing device was employed, which makes use of a very wide second slit, the velocity corresponding to a line at a distance l from the bottom of the film is

$$V \text{ (volts)} = \frac{H^2}{8 \cdot 10^8} \cdot \frac{e}{m} \{a^2 + (b+l)^2\}$$

a = distance between the two slits.

b = distance from the centre of the second to the bottom of the film.

Fig. 2.



In the final apparatus the second slit was also narrow and much closer to the first. In addition, the presence of the iron cylinder reduces very considerably the field in its immediate neighbourhood, and to a lesser extent over the whole region of the camera. Consequently, a being now effectively zero may be dropped out of the equation, b was measured and found to be 0·75 cm. The equation used was thus

$$V = K (\cdot 75 + l)^2.$$

The constant K being determined by calibration for the small range of the film which was actually used. This was done for two values of the magnetic field employing 13·20 and 16·28 gauss, the total applied potential being in the first case varied from 80 to 100 and in the second case in the neighbourhood of 150 volts. From these two measurements the two values of K were found in the usual manner. The error in the determination of differences can be estimated by observing that the first factor of

$$\delta V = 2K (\cdot 75 + l)\delta l$$

can be found to within 1 per cent., as shown by the values of V calculated from l, and the second part can also be determined to less than 1 per cent. The error to be expected in measurements of energy losses is thus somewhat greater than 1 per cent. The values given in Table I. bear this out fairly well, as most of them can be included within the mean value $\pm 0{\cdot}2$ volt.

When the adjustment of the cathode with respect to the camera slit system is satisfactory and no gas is present in the collision space, then, as can readily be seen, the single lines obtained corresponding to the applied accelerating potential will consist of two parts, which in general will be approximately superimposed. First, the electrons issuing from an almost point source move down towards the camera in very nearly straight lines, and the mark due to the direct beam will have a width limited by the length of the first slit, *i.e.*, 2 mm. Secondly, a number of electrons will suffer collision at the metal boundary or slit walls and may, in general, have all directions as they pass through the first slit; thus these will produce a line of uniform density stretching across the whole of the exposed part of the film. When gas is present this "uniform" line will be enhanced by the elastic, or almost elastic, collisions which occur with the gas molecules. As might be expected, it was only in exceptional cases that the alignments (including in addition that of the magnetic field) were sufficiently accurate to bring the part due to the direct beam into the centre of the film. The portion due to the direct beam is very much more intense than the second part and, as indicated here, is usually slightly higher up the film, but by an amount which is certainly not more than a few tenths of a volt. It is, however, a point of considerable interest, since in almost all the photographs which have been measured or photometered, the intense part due to the direct beam was at either one or other edge of the uniform line, and, consequently, all measurements referring to losses are made to the centre, *i.e.*, the point of maximum intensity of this last-mentioned part, and may thus be less than the true value by any amount up to 0·4 volt. With hydrogen present at the pressures usually employed, this line should be due mainly to electrons which have been reflected from the surface of the metal walls rather than to electrons which have suffered collision with the gas molecules: but for those cases in which the alignment was accurate, the uniform part of the full velocity line line must arise from electrons scattered by the gas, since any reflected at the cylinder walls would subtend too great an angle to

register on the film. This is borne out by the fact that, in such cases, the uniform portion of the line is of the same order of intensity as the line due to electrons which have suffered effective collision. From this it follows that the numerical value of the loss at high voltages given in Table I. can only be regarded as setting a lower limit to the energy loss, the upper limit, however, being not greater than 0·4 volt beyond this value. Fortunately, less ambiguous results can be obtained for the true amount of energy lost by fast electrons from the photographs showing the effect of double collision—a point mentioned later in more detail.

Results.

The photographs obtained with hydrogen can most easily be described by considering them in three groups.

(1) Those obtained with high electron velocities, above 50 volts and moderate gas pressures, *i. e.*, not greater than 10^{-2} mm. Hg.

(2) Those obtained at high velocities about 150 volts and higher gas pressures of the order of 3×10^{-2} mm. Hg.

(3) Those obtained with low velocities, below 25 volts, and moderate pressures.

Table I.

Photo.	Pressure, mm. Hg.	Velocity in collision space, volts.	Total final velocity, volts.	Energy loss, volts.
1	0·007	16	91·0	12·13
2	0·009	17	93·2	12·38
3	0·011	17	92·0	12·53
4	not measured.	24	98·0	12·18
5	,,	24	98·0	12·08
6	,,	24	97·8	12·03
7	0·009	25	97·0	12·21
8	0·009	26	89 0	12·53
9	0·009	30	103·8	12·31
10	0·008	50	98·0	12·22

Mean Energy loss=12 26 volts.

(1) Of these photographs a number were chosen which appeared the most suitable for measurement, both on account of the clearness of the lines and because of the definiteness with which the conditions of the exposure were known, and the results of the measurement of all these are given in Table I. The loss given here is the only one which appears with certainty on photographs taken at high velocities: it also appears, however, at low velocities, and, consequently, the measurements given are not restricted merely to the former case. It may be that part of the small variations to be observed in Table I. is due to the distance between the points of maximum intensity of the full velocity line and of the loss line expressed in volts actually varying slightly under different conditions, a variation due perhaps to the small losses of energy which the electrons suffer either in collision with the gas molecules or by reflexion at the metal surfaces during "elastic" collision. Photographs taken with high electron velocities and low gas pressures all show a single well-defined loss line of considerable intensity, in addition, of course, to the full velocity line. It appears hardly necessary to mention that what may be called purely instrumental effects such as lack of uniformity of the magnetic field, fall of potential down the filament, contact potential differences and such like, cannot directly affect the magnitude of the energy differences. To the low velocity side of this 12 volt loss line, as appears on some of the photometric curves, there is an indication of another line or edge at about 14 or 15 volts. This corresponds possibly to the edge of the continuous absorption spectrum as given by Dieke and Hopfield at 14·53 volts, and is considered later.

(2) The photographs obtained in this group at high gas pressures were intended primarily to furnish values of the excitation probability at high velocities (see p. 902), but they can also be used to provide the correction for the error which is introduced by the slight uncertainty of the full velocity line. These photographs (one of which is reproduced) show two loss lines: the first very strong, being the one already considered, which arises from electrons having suffered a single effective collision; the second being due to electrons which have suffered two such effective collisions. The true value of the energy lost by the electron in this particular type of collision will be given by the voltage separation between the first and second loss lines, whilst the difference between the first and the full velocity line will give

a value like the mean of Table I. Measurements made on five photographs of this sort showed that the true energy loss was 0·36 volts greater than the mean value of the separation between the first loss and the full velocity line. The resulting value of the energy lost in collision is then 12·6 volts to within the accuracy of these experiments, which may be estimated for the mean as about 1 per cent.

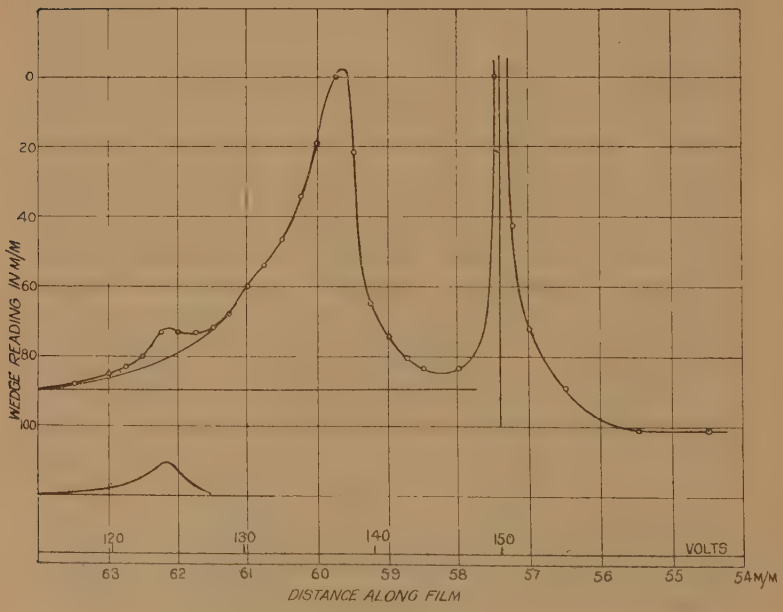
(3) Photographs obtained at low excitation velocities differ from those taken at high velocities, the change being a gradual one as the accelerating potential is reduced.

In this apparatus, where only the electrons which are flung forward through a very small angle are examined, the change is first to be observed at approximately 26 volts. At this potential a faint line appears at a distance corresponding to a loss of 9·1 volts. Naturally as the line is faint at this voltage, the accuracy of the measurement is small, and the value given might be in error by a few tenths of a volt. At lower potentials the intensity of this line increases very greatly, until at 18 or 16 volts it is comparable in intensity with the line at 12·6 volts. At still lower potentials from 13 to 14 it again vanishes, a number of photographs being obtained at these very low potentials, and on none, although the 12·6 line can always be seen, does the other appear. When the velocity was below that required to stimulate the 12·6 loss, the photographs showed only the single line corresponding to the applied accelerating potential, but to the low velocity side of this there was, in general, a very faint shading extending a distance of some 4 or 5 volts. At potentials about 16 volts, *i. e.*, the lowest at which this second loss occurred strongly, there exists shading between this line and the full velocity line. The point of maximum intensity corresponding to this loss does not appear to be a definitely fixed value independent of the excitation conditions. The photographs (1, 2, 3, and 23) show this line strongly and clearly, and the differences in the value of the loss are certainly due to the actual displacement of the point of maximum intensity. That this displacement is due to extraneous causes is made untenable by the fact that the measurements of the 12·6 (or direct mean 12·26) line on the same photographs give normally good values. These results are not as surprising as may at first sight appear when it is observed that this loss is probably connected with the dissociation of the molecule. Table II. gives the loss in volts corresponding to the maximum of this line. The measurements for this table have been taken from

TABLE II.

Photo.	Pressure, mm. Hg.	Velocity in collision-space, volts.	Total velocity, volts.	Loss, volts.	Ratio of Intensities.
23	0·007	16	90	8·64	
1	0·007	16	91	7·30	0·24
2	0·009	17	93·2	8·62	0·13
3	0·011	17	92	8·13	0·17
24	0·010	18	81·5	9·03	
8	0·009	26	89	9·59	0·03

Fig. 3.



photometric curves similar to fig. 3 which has been obtained from the spectrum reproduced above.

Besides the determination of the energy-loss, estimates have been made of the relative intensities of the two "lines" for a few different voltages. This has been done by comparing the areas under the two maxima on the photometric curves corresponding to the 12·6 and the lower loss.

As the photographic effect of slow electrons occurs through the intermediary action of the fluorescent grease

with which the films are sensitized, the intensity of the blackening will be related to the number of electrons in the beam, in the same way as the blackening depends upon the intensity of light in the ordinary case. If the blackening is not too intense, the photographic density may be taken as proportional to the intensity of the incidental light. Since the distance along the wedge of the photometer employed is proportional to the photographic density, and as the ordinates of the photometric curves are just the wedge-readings, these will be proportional to the number of electrons in the beam producing the mark. Thus the relative number of electrons having suffered the 12·6 and the lower loss will be given directly by the ratio of the areas on the photometric curves under their respective maxima. In the last column of Table II. are given the values of these ratios for a few cases. The photographs from which these ratios were obtained differed from those taken for ordinary energy-loss measurements only in that special care was taken to obtain a perfectly steady thermionic current and to measure this and the time of exposure (usually 4 or 5 minutes) accurately. The greatest difficulty in making measurements of intensities was that of obtaining a suitable reference line on the photometric curves. During an exposure the whole of the film is slightly darkened by electrons which are scattered within the camera. Moreover, all those electrons which are scattered near the slits (and most of them should be, since the gas is leaking through this way into the camera) will strike the film somewhere below the line corresponding to the applied potential. Consequently, it does not appear justifiable to use the flat part of the curve beyond the full velocity line as the reference level, rather should that part be regarded as the true zero which becomes flat below the loss line. In the treatment of the graphs, such as that shown, the centre of the full velocity line was first drawn, being determined from the upper part of the corresponding peak. This latter was then made symmetrical and the right-hand side of the first loss peak constructed by subtracting the ordinates. The left-hand part of this peak was then extrapolated to the base-line, and the right-hand side of the second loss peak determined as in the first case. For the curves referring to photographs taken at high velocities for the determination of the probability of excitation in which the second line is much fainter than the first, the adopted method was to extrapolate the curve of the first line, subtract the ordinates, and construct the curve of the second line from these. In addition, it is known that the second curve must be of the same form as the first, with

the ordinates diminished in a certain constant ratio. This serves as a check on the extrapolation.

Determination of the Probability of Effective Collision.

Although at the present time there are a few quantitative results on the probability of excitation by electron impact for electron velocities in the neighbourhood of the excitation potential, yet there appears to be no data giving the value of this probability for velocities exceeding the critical potential by some 100 volts. Seeliger and his collaborators have determined the relative excitation probabilities (or quantities closely allied) for these velocities by spectroscopic means. The experiments described here give a direct method for measuring the value of this probability at high velocities. Results are given for the A→C transition of the hydrogen molecule at a velocity of 150 volts.

The essential feature of the method is the obtaining on a single photograph of two lines, one due to electrons which have suffered a single effective collision, the other to electrons which have suffered two effective collisions. As will be readily seen, the ratio of the intensities of these two lines, a knowledge of the gas-pressure and the path-length, is sufficient to determine the absolute value of the probability of excitation.

The work of Lenard and others shows that a fast electron is deflected from its path or loses energy when it passes within the boundary determined by the gas kinetic radius of the molecule. This is equivalent to putting the mean free path of a fast electron equal to $4\sqrt{2}$ times the molecular mean free path.

Now let p be the probability that an encounter (as just defined) shall result in the stimulation of the molecule to a certain state, and the flinging off of the electron in approximately the same direction as that of approach. If the path-length in the gas be d the probability that an electron shall suffer one and only one encounter is $\frac{d}{\lambda} e^{-\frac{d}{\lambda}}$, where λ is the electron mean free path. Thus for the intensity of the first line we put

$$I_1 = \text{const. } p \cdot \frac{d}{\lambda} e^{-\frac{d}{\lambda}}.$$

The probability that an electron shall suffer its first encounter between x and $x+\delta x$, lose energy, and be flung off in the same

direction is $pe^{-\frac{x}{\lambda}}\frac{\delta x}{\lambda}$. The probability that it shall then suffer one and only one encounter in the remaining distance is $\frac{d-x}{\lambda}e^{-\frac{d-x}{\lambda}}$. Multiplying together and integrating from 0 to d, and multiplying by p, we have for the intensity of the second line

$$I_2 = \text{const. } p^2\frac{d^2}{2\lambda^2}e^{-\frac{d}{\lambda}},$$

the constant in each case clearly being the same.

$$\therefore p = \frac{2\lambda}{d}\cdot\frac{I_2}{I_1}.$$

The quantity p which is determined by the experiment is not the true excitation probability ; but for high electron velocities it approaches this within 1 or 2 per cent. as the results of Langmuir and also of Dymond show. This conclusion can also be drawn from many of the photographs obtained in these experiments. As already explained, when the alignment is such as to bring part of the direct beam into the camera, there is produced a short, very intense line, superimposed on the uniform part of the full velocity line It is found that there is a corresponding increase of intensity in the 12·6 loss line at the same position. The meaning of this clearly is that the beam composed of the electrons which have lost 12·6 volts, expands only a little at high velocities from the original full velocity beam. In other words, most of the electrons are flung through only a very small angle when suffering effective collision at high velocities.

Table III. gives the values of the excitation probability taken from the only photographs which were photometered. It appears that it is of the order of 1 or 2 per cent. The mean of the first four values relating to an electron velocity of 150 volts is 0·015.

Relation between the Energy Losses of the Electrons and the Spectroscopic Term Values of H_2.

The result of an electron impact with an atom, as far as energy interchanges are concerned, can be given a straightforward interpretation. The energy lost by the electron is very nearly equal to the energy difference between two states of the atom. In the case of an impact with a molecule,

it is still true, of course, that the energy is conserved, but that gained by the molecule will in general be distributed between the electronic and the nuclear states. The process of excitation, according to Franck *, occurs in the first place by the change of the electronic state, the nuclear motion being affected only indirectly as a result of the sudden change of binding. This picture has been justified to some extent by Condon †. When the stimulation occurs by the impact of a fast electron, say of 100 volts or more, it is to be expected that the molecule will be raised to some higher electronic state and that the primary electron will have lost this energy and passed on before the nuclei respond to the altered binding. Thus it is to be expected that the energy lost by a fast electron in collision with a gas-molecule will be equal to the change of energy due to the transition of the

Table III.

Photo.	Velocity, volts.	Ratio of Areas.	Pressure ‡, mm. Hg.	Excit. Prob. p.
18	150	0·053	0·0275	0·011
19	150	0·073	0·0204	0·020
20	150	0·056	0·0207	0·015
21	150	0·057	0·0255	0·013
22	98·8	0·060	0·0245	0·014

electronic state plus vibrational energy of an amount corresponding to the potential energy of the two nuclei in the higher electronic state, but with their original separation.

In order to estimate the amount of the vibrational energy imparted to the molecule, one only needs to draw the curve showing the energy of the molecule in a particular electronic state for various separations of the nuclei. When the band spectrum has been sufficiently analysed so that the vibrational and rotational constants are known, it is possible to do this for small values of $(r-r_0)$, where r_0 is the equilibrium

* Franck and Jordan, *loc. cit.* p. 252.

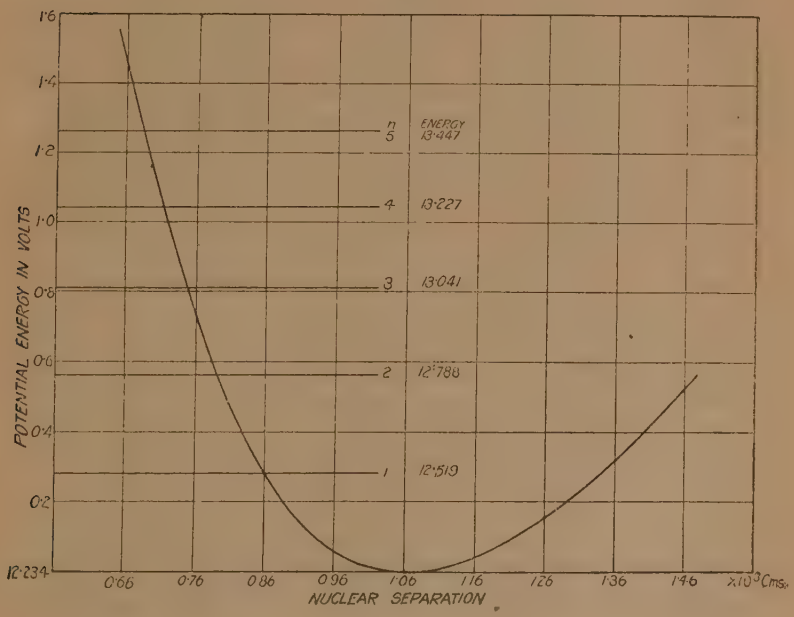
† Condon, Proc. Nat. Acad. Sc. xiii. p. 466 (1927).

‡ Owing to the smallness of p, the gas-pressure was raised in these experiments to the greatest practicable value so as to make λ as small as possible. This greatest pressure was found to be about 0·03 mm., the limit being set by the necessity of (1) preventing too rapid a leak through the slit into the camera; (2) providing the filament with a reasonably long life; (3) guarding against too frequent arcing between filament and grid.

separation. If the force between the two nuclei be expanded as a power series in $(r-r_0)$ the first three coefficients k_1, k_2, k_3 can be obtained from the band constants. Using the numerical data recently collected by Birge *, fig 4 referring to the C state of H_2 has been drawn showing the relation between the potential energy and the nuclear separation.

It is seen that when the nuclear separation in this state is equal to that in the normal A state, *i. e.*, 0·76 A.U., the potential energy due to the displacement of the nuclei

Fig. 4.



$=0·74$ volt. It appears, then, that a collision with a fast electron resulting in the transition to the C state will involve the stimulation of vibrational motion and that the most probable values of the vibrational quantum-numbers are $u=2$ or 3. The point of maximum intensity on the photographs would be expected, therefore, to correspond to a loss of some value between 13·0 and 12·78, the precise position depending on the relative numbers which lose one or other of these values. Actually the adopted mean from the given measurements lies at 12·6 volts, but this is sufficiently near

* Birge, Proc. Nat. Acad. Sc. xiv. p. 12 (1928).

to make it likely that this line is rightly allocated to the C state. Still more convincing evidence on this point is that Hori, when examining the ultra-violet emission spectrum of H_2 stimulated by electrons of velocity varying up to 200 volts, found that only the bands corresponding to the C→A transition were emitted at all strongly. It is noteworthy that unless there be some factor in the process of excitation by electron impact which tends to make one, or perhaps two, neighbouring vibrational levels much more probable than the rest, then our photographs would not show anything like a line at all, since the vibrational levels of the C state, according to Dieke and Hopfield * extend from 12·23 to 14 53 volts.

The complete absence of any line at 4·34 volts for high electron velocities may be regarded as additional direct evidence for the already well-established fact that high-velocity electrons are ineffective for producing dissociation by direct means, *i. e.* by yielding up just sufficient energy to carry this process out without simultaneous excitation of some electronic state.

A review of the older work on the measurement of critical potentials in hydrogen reveals, at all events, one feature which appears reliable, in that it is common to most observations. This is the existence of a strong radiation potential in the neighbourhood of 12·6 to 12·9 volts. It is to be remembered that the energy losses measured in this way are those sustained usually by electrons whose velocity is in the immediate neighbourhood of the excitation potential considered. Nevertheless, since the photographs obtained at low velocities (13 or 14 volts) still show the line corresponding to the A→C transition (though of much reduced intensity), it appears that the above-mentioned critical potentials arise in the same way as the lines on our photograph, *i. e.*, by stimulation to the C state.

As already mentioned, at high velocities, apart from the 12·6 volt line (and the shading to the low-velocity side), there appears nothing else of noticeable intensity. Now the next lowest after the ground state is the $2\,^1S$ state, or the B of Dieke and Hopfield's notation. The non-vibrating level of this lies at 11·1 volts beyond the normal state. It appears, then, that the excitation of this state must be relatively very infrequent. This is in agreement with Hori's observation that the Werner bands always appear much more strongly than the Lyman bands even at low velocities. As

* Dieke and Hopfield, *Zs. f. Phys.* xl. p. 299 (1926).

a reason for this, it may be suggested that since the equilibrium separation of the nuclei for the $2\,^1S$ state is 1·55 A.U., and that of the normal $1\,^1S$ state 0·76 A.U., when excitation to the $2\,^1S$ state occurs by the action of a fast electron, the potential energy imparted to the nuclei, as a result of the altered binding, will be great, corresponding to a displacement of 0·79 A.U. Thus, if an impact with a fast electron is to result in the transition to the B electronic state, then this must be accompanied by the stimulation of a vibrational state of high quantum-number, or more likely by dissociation. Now according to Dieke and Hopfield, the limit of the B state is common with that of the C state, and lies at 14·53 volts. It would thus appear that is the significance of the increased intensity in the shading to the low-velocity side of the 12·6 volt line lying at 14 to 15 volts, which is especially prominent on the photographs taken at high velocities, as appears from the photometric curves. The products of the dissociation at 14·53 volts are given by Dieke and Hopfield as a neutral atom and an atom in the first quantum state, *i. e.*, the 10·15 state, this giving a value of 4·38 for the dissociation potential. If the energy imparted as a result of the collision be somewhat less than 14·5 volts, the molecule may be left in the B state with strong nuclear vibration. It is generally considered that returns from such states to the ground A state will result in dissociation and the emission of the continuous spectrum. In a word, then, collisions of fast electrons resulting in the stimulation of the B state might be expected, first, not to require 11·1 volts, but something in the neighbourhood of 14, and, secondly, to result not in the stimulation of the Lyman bands, but rather in that of the continuous spectrum.

The photographs obtained at low velocities appear to be rather surprising, but the large number taken under various conditions, and even with different forms of apparatus, forces one to the conclusion that low speed electrons may lose energy as a result of collision with some form of hydrogen of an amount much greater than the dissociation potential, but less than the first excitation stage of either the atom or the molecule. Moreover, for given conditions (mainly the accelerating potential) there is one value of the energy loss much more probable than any other. This is shown by the maximum to be seen on the photometric curves. It is especially to be noticed that when the accelerating potential is less than 14 or 15 volts, this loss of energy does not occur with sufficient frequency to produce a noticeable line on the photographs. Thus it would appear possible for it to be made

evident by the critical potential methods, since the number of electrons losing this energy increases gradually as the velocity is increased, without there being any well-defined threshold potential.

It was at first suggested * that this effect might correspond to the excitation of H_3, as relatively large quantities of H_3^+ are known to exist under the discharge conditions employed. The rare appearance of the loss below about 15 volts suggested that H_2^+ was in some way connected with its occurrence, and this it is known is necessary to the formation of H_3.

It seems more likely, however, that this line appearing at low velocities is intimately connected with the dissociation of the diatomic hydrogen molecule. The fact that the most probable loss, *i. e.*, the loss corresponding to the point of maximum intensity, is not a definite amount, but increases as the velocity of the primary electrons increases from 16 to 20 volts, makes it unlikely that it corresponds to any particular excitation state of any kind of molecule.

When the initial velocity of the electron, suffering collision with the molecule, corresponds very nearly to the energy separation of the two states between which the transition occurs, it might be expected that the electron and molecule will remain in interaction for a time sufficiently long to allow the nuclear motion to affect the amount of energy finally lost by the electron. The energy lost under consideration may be due, therefore, to an excitation process, which finally results in the dissociation of the molecule and the emission of radiation which forms part of the continuous spectrum. It is interesting to notice in this connexion that Oldenberg † has found that the continuous spectrum, but not the Lyman bands, is strongly excited by electron impacts in pure hydrogen, but when argon is present Lyman bands appear strongly and the continuous spectrum very weak. The two thus appear to be closely related and probably due to the same initial electronic excitation, *i. e.*, to the B state. The essential difference is, according to Oldenberg, that with argon present (the excitation occurring then by collisions of the second kind with the excited argon atoms) the vibrational energy is limited to that of the third state, whilst in the other case high vibrational states may occur, and therefore dissociation in the resulting transition which produces the radiation of the continuous spectrum. The work of

* Jones and Whiddington, Proc. Leeds Phil. & Lit. Soc., July 1928.
† Oldenberg, *Zs. f. Phys.* xli. p. 1 (1927).

Hughes and Skellett* shows that dissociation occurs almost certainly as a result of a simple process, *i. e.*, not a secondary effect, and, moreover, that the dissociation does not set in until the electrons have a velocity of 11 or 12 volts, and increases for higher potentials. These results fit with the observation first made by Horton and Davies† of the excitation of the continuous spectrum at low velocities. They gave tentatively as the lower limit for excitation 12·6 volts.

Finally, then, it appears that (1) the loss not being a definite one, independent of the excitation conditions, suggests that it is connected with dissociation; (2) results like those of Hughes and Skellett indicate that dissociation is connected with the emission of the continuous spectrum, since there appears no other way of accounting for the balance of energy, and does not occur until the electrons have a velocity of about 12 volts; (3) Oldenberg's results may be taken to indicate that the continuous spectrum is intimately connected with the excitation of the B electronic state, and this, as has been previously mentioned, would apparently require the impacting electron to have an initial velocity somewhat greater than the 11·1 volts necessary to stimulate the B_0 state. This fits, then, with the non-occurrence of the loss at very low potentials, and may be taken to support the attribution of this loss to a dissociation process.

Summary.

Experiments are described in which the energy losses of electrons in hydrogen of controllable velocity are measured, and also the relative number in the different energy groups. The results of the measurement of the photographs and their photometric curves may be summarized as follows:—(1) By far the most probable effect of a collision between an electron of 50 volts or more velocity and a hydrogen molecule is the excitation of the C state with a certain amount of vibrational energy. (2) The probability of effective collision at 150 volts is in the neighbourhood of 1 or 2 per cent. (3) At low velocities, smaller losses, the upper limit of which is 8 or 9 volts, varying slightly with the primary electron velocity, are observed, and the suggestion is made that these are connected with the dissociation of the molecule and the excitation of the continuous spectrum. (4) There is no loss of about 11·1 volts to be found, indicating that the B_0 and other low vibrational B states cannot be stimulated directly

* Hughes and Skellett, Phys. Rev. xxx. p. 11 (1927).
† Horton and Davies, Phil. Mag. xlvi. p. 872 (1923).

by electron impact. (5) There is no indication, except at very low velocities (8 to 10 volts) when it is very faint, of a loss occurring which might be connected with direct dissociation.

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The University, Leeds.

LXXXIX. *The K X-Ray Absorption Edge of Iron.*

By Geo. A. Lindsay *and* H. R. Voorhees *.

[Plate XVI.]

Introduction.

RECENT work in X-ray absorption spectra has shown that on the short wave-length side of the edge there often exists a complicated appearance which has been called the fine structure, or multiple structure of the edge. Early investigators were Stenström †, Fricke ‡, and Hertz §. Lindh ‖, in an extended study of the K absorption edges of sulphur, chlorine, and phosphorus, found one or two secondary edges. Coster and Van der Tuuk ¶ reported a secondary edge very close to the K edge of argon. Van Dyke and one of the writers ** found a more complicated structure for the K edge of calcium than had previously been observed for any element. Nuttall ††, working in this laboratory, has recently shown a structure for the potassium and chlorine K edges which is also very complicated.

The valence of the element affects the position of the absorption edge. In the work of Lindh there appeared a progressive shifting of the edge towards shorter wave-lengths as the valence of the element became higher.

The present work was undertaken for the purpose of extending the knowledge of the structure of the K absorp-

* Communicated by J. M. Nuttall, M.Sc.
† Stenström, Diss. Lund, 1919.
‡ Fricke, Phys. Rev. xvi. p. 202 (1920).
§ Hertz, *Zeits. für Phys.* iii. p. 19 (1920).
‖ Lindh, Diss. Lund, 1923.
¶ Coster and Van der Tuuk, *Zeits. für Phys.* xxxvii. p. 367 (1926).
** Lindsay and Van Dyke, Phys. Rev. xxviii. p. 613 (1926).
†† Nuttall, Phys. Rev. xxxi. p. 742 (1928).

tion region and also with the hope of showing the effect of valence on this structure. With this in view, iron was chosen because of its convenient wave-length, because of the fact that crystals containing iron are plentiful, and also because iron has two valencies.

Experimental Procedure.

Two methods were used to obtain the absorption: first, crystals containing iron were used both as diffracting crystal and as absorbing medium; second, screens were made and placed in the path of the beam in the usual manner. The first method has the advantage of forming a very uniform absorber, and of permitting more radiation to reach the plate. It is a very desirable method for long wave-lengths and when good crystals are obtainable. On the other hand, if the crystals are poor and if suitable absorbing screens can be made, the second method gives better results. While crystals containing iron are plentiful, they have not especially good surfaces, and hence in this work the better results were obtained by the second method.

Many of the crystals used were not common in X-ray work, and it was therefore necessary to obtain the crystal-grating constants. This was done by precision measurements on the CuKα line, as outlined by Siegbahn *. The natural faces of the crystals were used, but in some cases these were polished in an effort to eliminate some of the surface irregularities. This polishing no doubt sacrifices to some extent the sharpness of the fine structure. The absorbing screens were made by mixing the finely-pulverized compound with collodion and spreading the mixture out in thin films to dry. In this manner screens of suitable thickness could readily be obtained. One of the crystals used in the first method was lepidomelane, a mica which contains iron, and which can be split into sheets as thin as 0·01 mm. These sheets served as excellent absorption screens for the second method. The screens for metallic iron were made by rolling a piece of pure electrolytic iron which was obtained from the General Electric Co., through Professor W. P. Davey. The rolling was done between pieces of copper, and fairly uniform screens as thin as 0·01 mm. were made.

A sylvite (KCl) crystal was used in the absorbing screen method. This crystal gave very good reflexion. Its dispersion is somewhat greater than that of calcite.

* Siegbahn, 'Spectroscopy of X-Rays,' pp. 62-64.

A Siegbahn vacuum spectrograph was used for photographing the edges. The reference line used on all the plates was the FeKβ line. The WL_2 line was also near, and served as a check. The distance from absorption edge to reference line was measured on a comparator having a least count of 0·005 mm.

In measuring the edge the cross hair of the comparator microscope was brought up just to the point where the blackening begins to decrease. The practice has commonly been to add to this reading one-half the width of the slit. It was found, however, that this correction gave abnormally low wave-lengths in cases where the dispersion of the crystal was small. If no corrections were made, the values for the edge by the two methods were found to agree much better. It was also found that the edge was much less sharp for metallic iron than for the compounds, even though other conditions were the same. This shows that factors other than slit-width may determine the sharpness of the edge. From these considerations it was thought best to omit the correction for the width of the slit. The width of the slit in the crystal method was 0·126 mm. In the screen method, where stronger reflexion could be obtained, it was narrowed to 0·043 mm. This aided in the resolution of some of the details of the structure.

The curves shown in this work are microphotograms taken on a Moll microphotometer. The lens system was modified so as to utilize more of the height of the plate, thus eliminating most of the fluctuations due to the coarse grain of the X-ray plates.

Experimental Details.

The predominant features of the multiple structure are as follows: first, a very sharp principal absorption edge; second, an intense white-line absorption immediately to shorter wave-lengths; third, several secondary regions of absorption, which also sometimes appear as white lines of less intensity. The more striking appearance of the first white line is, however, partly due to the fact that there is less contrast at the secondary edges. The microphotograms show that in many cases the secondary absorptions are really as intense as the principal white line. The blackening between the secondary absorptions by no means approaches in intensity that on the long wave-length side of the principal edge. In the tables this principal edge, which is the one always measured, is designated simply as the K edge. It forms the long wave-length boundary of the principal white line. The short

wave-length boundary is far less distinct. The secondary edges, that is the long wave-length sides of the secondary white lines or bands, are denoted by K_1, K_2, K_3, etc. Certain faint and narrow absorptions that are often found near the secondary edges are designated as K_1', K_2', etc. K_1' is between K and K_1, K_2' is between K_1 and K_2, and so on. The structure is quite similar for all the compounds of iron.

The structure for metallic iron differs from that for the compounds in that the principal edge is less sharp, as is revealed by the microphotogram of fig. 3 (Pl. XVI.), and there is no white line absorption of note until the K_2 edge is reached. The multiple structure covers a much greater range than in the case of the compounds.

Results of the Crystal Method.

The following crystals were used as diffracting crystals and at the same time as absorbers :—

(1) Iron pyrites, FeS_2; (2) Arsenopyrite, AsFeS; (3) Hematite, Fe_2O_3; (4) Epidote, $HCO_2(Al, Fe)_3Si_3O_{13}$; (5) Lepidomelane, $(K,H)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3$; (6) Magnetite, Fe_3O_4.

A summary of the results of the crystal method is given in Table I. The values shown for any one crystal are the average from several plates. The fainter edges are given in parentheses. Fig. 1 (Pl. XVI.), shows a representative plate of this method taken with iron pyrite. In the reproduction of the plate fainter detail is perhaps not evident, but it may be seen in the accompanying microphotogram of the same plate.

The summary of the data shows that the bivalent iron, as it occurs in iron pyrites and arsenopyrite, gives the same wave-length value for the principal edge. The white line for these two compounds measured 7 x.u. in width. Close study of the clearer plates shows, however, that this white line is separated in the middle by a very narrow black line. This indicates the presence of a K_1' edge in this mid-position. Such an edge was found later for the bivalent iron in the absorption-screen method. This faint K_1' edge is probably less distinct in the crystal method because of the wider slit used in that method. The remaining structure of these two crystals is quite the same for both, except that the pyrite crystal, which gave the better reflexion, shows the K_2' and K_3 edges faintly, while in the other they cannot be detected. The hematite and epidote crystals contain trivalent iron. The wave-length of the principal

TABLE I.—Summary of Data for Crystal Method.

λ = wave-length in x.u. ΔV = energy difference in volts.

Crystal.		Edges, K.	White-line width.	K_1'.	K_1.	K_2'.	K_2.	K_3'.	K_3.	K_4'.
Pyrite, FeS_2 (Val. = 2).	λ	1738·7	7·1 (4·4)*	(1733·2)	1724·4	(1718·2)	1710·9	...	1698·5	1687·5
	$\Delta\nu/R$	..	2·15 (1·33)	(1·67)	4·34	(6·25)	8·52	...	(12·4)	15·9
	ΔV	...	29·2 (18·0)	(22·6)	58·9	(84·7)	(15)	...	(168)	215·0
Arseno-pyrite, $AsFeS_2$ (Val. = 2).	λ	1738·7	6·7 (4·0)*	(1732·8)	1723·9	...	1712·4	1707·9	...	1687·1
	$\Delta\nu/R$	...	2·03 (1·21)	(1·79)	4·50	...	8·05	9·45	...	16·0
	ΔV	...	27·5 (16·4)	(24·2)	61·0	...	109·0	128·0	...	217·0
Hematite, Fe_2O_3 (Val. = 3).	λ	1737·2	4·3	...	1725·8	...	1711·5	(1707·0)	...	(1686·6)
	$\Delta\nu/R$	..	1·30	...	3·47	...	7·88	(11·2)	...	(15·7)
	ΔV	...	17·6	...	46·9	...	107·0	(151)	...	(213)
Epidote (Val. = 3).	λ	1737·2	4·6	...	1726·1	...	1713·3	...	1696·2	...
	$\Delta\nu/R$	...	1·39	...	3·38	...	7·32	...	12·7	...
	ΔV	...	18·8	...	45·7	...	99·0	...	172	...
Lepidomelane (Val. = 2 & 3).	λ	1737·5	4·6	...	1723·5	...	1714·1	1709·4	1695·9	1689·7
	$\Delta\nu/R$	...	1·39	...	4·26	...	7·16	8·62	129	14·8
	ΔV	...	18·8	...	57·8	...	97·0	117·0	174	201·0
Magnetite (Val. = 2 & 3).	λ	1737·6								

Faint signs in parentheses.

* Probable separation point in the white line; barely discernible.

edge for these crystals was 1·5 x.u. shorter than for the bivalent forms. The white line was here found to be 4·4 x.u. in width.

The lepidomelane and magnetite crystals contain both bivalent and trivalent iron. The reflexion from the magtite crystal was so poor that only the principal edge could be measured. The lepidomelane gave very strong reflexion, but its grating constant was large, and the dispersion was only 55 x.u. per mm. The detail was as sharp as in the crystals having iron of only a single valence.

Results of the Absorption-screen Method.

The absorption-screen method was more fruitful of results because of the excellent reflexion of the (K Cl) crystal used. The slit was now narrowed in order to aid resolution. The dispersion for this sylvite was slightly greater than for calcite.

Absorbing screens were made of the following compounds:—ferrous carbonate, $FeCO_3$; ferric oxide, Fe_2O_3; ferrous ferric oxide, Fe_3O_4; ferric chloride, $FeCl_3 . 6H_2O$; ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 . 6H_2O$; and a mechanical mixture of the last two. Thin sheets of lepidomelane were also used as screens, and the metallic iron screen, made as described above, gave the absorption for the uncombined element.

The mineral siderite ($FeCO_3$) and ferrous ammonium sulphate were chosen because they are rather stable compounds.

Table II. shows a summary of the data obtained by the absorption-screen method, while figs. 2 and 3 (Pl. XVI.) show plates of Fe_3O_4 and metallic iron respectively with their microphotograms. In the case of the mechanical mixture it may be seen that the principal edge is like that for bivalent iron. We should expect this, for if the structures due to both forms are present, the edge due to the trivalent iron would fall in the intense white line due to the bivalent iron, and hence would not appear. Where the bivalent and trivalent iron are both in a single compound, as in the lepidomelane and magnetite, no evidence of a superposition of the two spectra could be found. The wave-length of the principle edge was intermediate between that for the two forms of iron. The white line was very narrow and a distinct K_1' edge was observed. These features indicate that the iron is held in these compounds in such a way as to show neither bivalent nor trivalent spectral characteristics. It rather appears that the iron ions are all alike.

TABLE II.—Summary of Absorption-screen Method. KCl. Crystal.

λ = wave-length in KCl. ΔV = energy difference in volts.

Screen.		Edges, K.	White-line width.	K_1'.	K_1.	K_2'.	K_2.	K_3'.	K_3.	K_4'.	K_4.	K_5.	K_6.
Ferric oxide, Fe_2O_3.	λ	1736·8	3·9	1731·7	1725·6	...	1713·3	..	1704·5	1686·5			
	$\Delta\nu/R$	...	1·18	1·85	3·41	...	7·20	...	9·9	15·6			
	ΔV	...	16·0	25·0	46·1	...	97·5	...	135·0	212·0			
Ferric chloride, $FeCl_3 . 6H_2O$.	λ	1736·8	3·5	1731·1	1725·5	..	1714·9	...	1707·1	1692·0	(1682·0)	(1665·7)	
	$\Delta\nu/R$	...	1·06	1·73	3·44	...	6·71	...	9·1	13·9	(17·4)	(22·4)	
	ΔV	...	14·4	23·4	46·6	...	90·8	...	124·0	18·8	(232)	(304)	
Ferrous carbonate, $FeCO_3$.	λ	1737·9	9·7	(1734·2)	1728·4	...	(1716·0)	...	1709·5	1689·5			
	$\Delta\nu/R$	...	·82	(1·12)	2·89	...	(6·69)	...	8·7	15·0			
	ΔV	...	11·1	(16·2)	39·1	...	(90·7)	...	118·0	203·0			
Ferrous ammonium sulphate, $FeSO_4(NH_4)_2 SO_4 . 6H_2O$.	λ	1737·4	2·7	1733·2	1728·0	...	1716·8	...	1706·2	1695·9	(1682·1)	(1662·4)	
	$\Delta\nu/R$	...	·82	1·27	2·86	...	6·30	...	9·6	12·8	(17·3)	(23·7)	
	ΔV	...	11·1	17·1	38·7	...	85·3	...	130·0	174·0	(234)	(321)	
Mixture of $FeCl.6H_2O$ & $FeSO_4(NH_4)_2 SO_4 . 6H_2O$.	λ	1737·5	3·6	...	1726·8	...	1716·5	...	1707·2	1695·2	(1683·2)	(1665·7)	
	$\Delta\nu/R$	...	1·09	...	3·25	...	6·42	...	9·3	13·1	(16·9)	(22·6)	
	ΔV	...	14·8	...	44·0	...	87·0	...	126·0	177·0	(229)	(306)	
Lepidomelane.	λ	1737·3	2·9	1732·1	1727·6	...	1713·8	1709·8	1699·3	1689·8	(1683·1)		
	$\Delta\nu/R$	...	·83	1·58	2·95	...	7·19	8·44	11·7	14·7	(16·9)		
	ΔV	...	11·9	21·4	39·9	...	97·4	114	159·0	200·0	(229)		
Ferrous-ferri oxide, Fe_3O_4.	λ	1737·4	3·3	(1731·9)	1726·3	...	1715·2	...	1704·7	1688·1			
	$\Delta\nu/R$	...	1·00	(1·67)	3·38	...	6·79	...	10·1	15·3			
	ΔV	...	13·5	(22·5)	45·6	...	92	...	136·0	208·0			
Fe, metallic.	λ	1739·3	...	1731·4	1726·7	1721·1	1715·2	1706·9	1701·3	1690·9	1683·4	1663·0	(1614·0)
	$\Delta\nu/R$	...	...	2·39	3·82	5·64	7·36	9·9	11·7	14·9	17·4	24·0	(40·7)
	ΔV	...	...	32·4	51·8	75·0	100·0	135·0	158·0	202·0	236·0	326·0	(551)

Values in parentheses are for faint edges.

Probably the most interesting portion of this work is the spectrum obtained with the screen of pure metallic iron. According to earlier views, which attributed the structure of the edge to the effect of the outer orbits, one should expect to find only a very limited structure for the absorption edge of a neutral element. On the contrary, our plates showed as many as a dozen secondary edges for metallic iron, the structure being distinct to more than 300 volts from the principal edge, with less distinct indications for several hundred volts further. This is a much greater range than has been observed before for the structure of any absorption edge.

It is of note that there is no white-line absorption at the principal edge for metallic iron. As may be observed from the photometer record of fig. 3 (Pl. XVI.), the slope of the edge is more gradual than for the compounds, and the K_1' and K_1 edges appear faintly on this slope. The first appearance of the usual white-line absorption is at the K_2 edge. The wave-length of the principal edge was found to be greater than for either of the ionized forms. Our value of 1739·3 x.u. for this edge is about 0·7 x.u. less than that given by Lindh.

Theoretical Considerations.

Kossel's theory of the fine structure was that the ejected electron may stop in the outer unoccupied orbits of the atom, and thus give rise to secondary edges, depending on the particular orbit in which the transition ends. The edge of shortest wave-length would thus correspond to complete removal of the electron, while the edge of longest wave-length would correspond to a transition to the innermost possible virtual orbit. This theory would account for a structure in the case of metallic iron of only a few volts in width, and at the most for not over 50 volts in the case of the trivalent Fe ion. The structure for the metallic iron here found is even more extended than for the compounds. We therefore think it very likely that multiple simultaneous ionization of the atom occurs under the action of the X-ray beam. G. Wentzel* predicted such a multiply-ionized condition in his discussion of the origin of certain non-diagram lines. Nuttall† gives this multiple ionization as the probable explanation of his results.

* G. Wentzel, *Ann. der Phys.* lxvi. p. 437 (1920).
† J. M. Nuttall, *loc. cit.*

When we attempt to calculate the position of any one of the secondary edges from the standpoint of multiple ionization, we find it difficult because of our lack of knowledge of the transition process in the outer part of the atom. However, since the portion of the spectrum corresponding to the virtual orbits is confined to a narrow region, it is possible to compute the *general* position of the absorption from a knowledge of the energy-levels of the atom.

If the iron atom has one of its K electrons removed to an outer level, its nucleus and K shell *together* then act, in so far as the outer electrons are concerned, like the corresponding parts of a cobalt atom. If an M electron were now to be ejected, it would require energy about equal to that for ejection of an M electron from a cobalt atom, which is about 104 volts for an M_I electron, 64 volts for an M_{II} or M_{III} electron, and 10 volts for an M_{IV} or M_V electron. If the K electron were entirely removed from the atom, these values would be somewhat more. Now, if one of these M electrons is ejected simultaneously with a K electron, the total energy absorbed will be approximately equal to the sum of that required to eject the K electron from the iron atom and the second M electron from a cobalt atom. If the M electron stops in some of the outer orbits, this energy value will be somewhat less. Thus, by choosing the proper number of electrons to be ejected and the proper stopping-places, it is possible to calculate values which will agree with almost any observed edge. The only point possible to make here at present is that that these computed values agree roughly with the structure found for iron. Thus the value for the K_1 edge is but slightly under the value computed for the ejection of a K electron together with an $M_{II\text{-}III}$ electron ; the K_2 edge is somewhat less than the computed value for the ejection of a K electron with an M_I electron. Further comparison is hardly worth while until more elements are investigated and until causes for variation in the fine structure are found.

From the multiple ionization viewpoint one might expect to find an absorption corresponding to the simultaneous ejection of a K and an L electron. Many trials were made with different absorption-screens and varying period of exposure to show such an effect. Several plates were obtained which showed two faint edges in the proper location to correspond to the ejection of an L_{II} or L_{III} electron with the K electron.

Kossel's theory will now be compared with the results obtained. According to tables of electron configuration, it

would appear that the N_{II} level is the first one in which a K electron might stop if the selection rule is obeyed. The absorption of energy sufficient to remove the K electron to this level may be considered as the cause of the principal edge. The energy necessary to remove the electron from this N_{II} level to infinity ought to be in the case of metallic iron about equal to the first ionizing potential for cobalt. The first ionizing potential of cobalt is given by Sur * as slightly over 8·5 volts. This would be the width of the virtual orbit effect, and if the white line is thus explained, it should not be more than this width for metallic iron. No evidence of a white line was found, but 8·5 volts would be equivalent to only about 0·2 mm. on our plates, and so narrow a white line might be practically obliterated by the radiation on either side. Applying the same reasoning to bivalent iron, it is found that the width of the white line should correspond approximately to the third ionizing potential of cobalt, which we are probably safe in assuming is not over 35 volts. This would be equal to a width of 8·5 x.u. If we ignore the division of the white line in the case of pyrite and arsenopyrite by the faint K_1' edge, then the entire width of the white line is about 7 x.u. The intense portion of the white line is much narrower than this.

Similarly, the limits for the virtual orbit effect for trivalent iron would be about equal to the fourth ionizing potential of cobalt, which we assume is not far from 50 volts. This is much greater than the observed width of the white line for trivalent iron. A width of 50 volts would reach about as far as the K_2 edge.

It may be, however, that the white line is only another manifestation of multiple ionization, since the second ejected electron might also stop in one of the innermost unoccupied orbits. We could then think of the principal K edge as corresponding to a complete ejection of a K electron, and of the white line as the additive effect of M electrons, moved to higher levels. This view of the principal edge, however, is not in conformity with the low values of $\Delta\nu/R$ for the interval between the L_I edge and the L_{γ_1} line obtained by Miss Chamberlain and Lindsay †. Andrewes, Davies, and Horton ‡ are also of the opinion that the principal absorption edge corresponds to the removal of the electron to the first possible unoccupied orbit.

* Sur, Phil. Mag. iv. p. 36 (1927).
† Chamberlain and Lindsay, Phys. Rev. xxx. p. 369 (1927).
‡ Andrewes, Davies, and Horton, Roy. Soc. Proc. cx. p. 64 (1926).

Summary.

The multiple structure for iron, both as a metal and in compounds, has been demonstrated to extend over a range considerably greater than that of any structure previously reported. The magnitude of this range is best explained by simultaneous ejection of electrons from outer orbits together with the K electron. Kossel's hypothesis appears satisfactory only as a possible explanation of the white-line absorption. As has been found previously, the principal edge shifts to shorter wave-lengths as the valence increases. The effect of valence on the multiple structure is small. When bivalent and trivalent iron are mechanically mixed, the expected superposition of the two patterns can be detected, but when the two valencies were in the same chemical compound, as in lepidomelane, no such overlapping could be found.

University of Michigan,
Ann Arbor, Michigan.
June 1928.

XC. *Measurements of the Velocity of Sound in Air, Nitrogen, and Oxygen, with special reference to the Temperature Coefficients of the Molecular Heats.*

By W. G. Shilling, *M.C., D.Sc., and* Prof J. R. Partington, *M.B.E., D.Sc.**

THE method of experiment and the apparatus used are essentially the same as those described in a previous communication †. Except in a few matters of detail, no further description is necessary. Description of the determination of the tube constant has necessarily been amplified in reply to adverse criticism of previous work ‡.

Preparation of the Gases.

Air.—The method of purification of the air used in the experiments is described in the previous communication §.

Nitrogen.—Nitrogen, containing as impurities only 0·3 per cent. (by volume) of oxygen and 0·1 per cent. helium and neon, was obtained from the British Oxygen Company.

* Communicated by the Authors.
† Phil. Mag. iii. p. 273 (1927).
‡ J. A. C. S. l. p. 627 (1928).
§ Phil. Mag. iii. p. 273 (1927).

The oxygen was removed by passage over reduced copper heated in a small electric furnace. The rare gases were not removed. The gas was dried by stick sodium hydroxide and phosphorus pentoxide.

Oxygen.—Electrolytic oxygen containing only 0·2 per cent. hydrogen was obtained from the British Oxygen

Table I.

Gases at Room Temperature.

No.	Air 20° C.		Nitrogen 19·5° C.		Oxygen 23·6° C.	
	Length.	λ/2 cm.	Length.	λ/2 cm.	Length.	λ/2 cm.
6	34·05	5 675	—	—	—	—
7	39·65	5·664	—	—	—	—
8	45·40	5·675	46·20	5·775	—	—
9	51·00	5·6 6	52·00	5·777	—	—
10	56·60	5·659	57·80	5·780	54·40	5·440
11	62·25	5·663	63·50	5·773	59·80	5·436
12	68·05	5 665	69·35	5·778	65·20	5·433
13	73·65	5·671	75·10	5·777	70·55	5·427
14	79·40	5·673	80·85	5·775	76·00	5·428
15	85·10	5·673	86·65	5·776	81·40	5·427
16	90·75	5·672	92·50	5·781	86·80	5·425
17	96·45	5·673	98·20	5·776	92·25	5·426
18	102·10	5·672	104·05	5·780	97·70	5·428
19	107·80	5·673	109·70	5·774	103·15	5·429
20	113·45	5·672	115·50	5·775	108·60	5·430
21	119·15	5·673	121·25	5·774	114·00	5·429
22	124·85	5·675	127·00	5·777	119·40	5·427
23	130 65	5·680	132·80	5·774	125·00	5·434
24	136·25	5·677	138·70	5·779	130·40	5·433
25	141·85	5·674	—	—	135·80	5·432
26	—	—	—	—	141·40	5·438
Means.....		5·671		5·776		5·431

Company. The hydrogen was removed by passage over heated platinized asbestos, and the gas then dried by calcium chloride and phosphorus pentoxide.

Measurements were then made, as described in the previous paper, at temperature intervals covering the range from room temperature up to 1100° C. Tables I. to III. give typical sets of measurements. The mean cold-junction temperature is given at the top of the table. The three columns for each gas contain the number of half wave-lengths, the corresponding mean half wave-length, and the temperature in

TABLE II.

Gases at about 460° C.

No.	Air 17·6° C		Nitrogen 17·4° C.		Oxygen 19·9° C.	
	λ/2 cm.	M.V.	λ/2 cm.	M.V.	λ/2 cm.	M.V.
0	—	3·920	—	3·798	—	3·930
5	—	—	8·898	3·762	8·370	3·965
6	8·810	3·974	8·889	3·882	8·367	3·985
7	8·815	3·974	8·887	3·862	8·368	3·985
8	8·817	3·935	8·894	3·864	8·374	3·995
9	8·820	3·980	8·895	3·890	8·378	3·965
10	8·825	4·005	8·897	3·870	8·373	3·955
11	8·828	4·005	8·901	3·844	8·382	3·920
12	8·830	3·975	—	—	8·380	3·970
Means...	8·821	3·971	8·894	3·846	8·374	3·963
C. J. ...		79		78		90
Temp....		4·050		3·924		4·053
		460° C.		446° C.		460° C.

TABLE III.

Gases at about 980° C.

No.	Air 15·8° C.		Nitrogen 17·2° C.		Oxygen 20·2° C.	
	λ/2 cm.	M.V.	λ/2 cm.	M.V.	λ/2 cm.	M.V.
0	—	9·940	—	9·758	—	9·800
4	11·319	9·950	11·892	9·760	10·760	9·905
5	11·321	9·917	11·910	9·810	10·764	9·930
6	11·324	10·015	11·927	9·960	10·760	9·950
7	11·321	9·960	11·930	9·860	10·803	9·945
8	11·330	9·910	11·930	9·800	10·804	9·900
9	11·336	9·820	11·918	9·790	10·784	9·805
10	11·332	9·800	11·899	9·785	10·787	9·815
Means...	11·326	9·914	11·915	9·815	10·780	9·881
C. J. ...		71		77		93
Temp....		9·985		9·892		9·974
		981° C.		973° C.		980° C.

millivolts respectively. At the foot of each table is added the cold-junction correction and the equivalent temperature in degrees centigrade.

The velocities of sound shown in Table IV. have been calculated from measurements over the whole temperature

TABLE IV.

True Velocities of Sound in metres per second.

Temp. °C.	Air.	Nitrogen.	Oxygen.
0	331·4	—	—
Room *	340·8	347·6	323·8
100	387·2	394·1	367·4
200	435·6	443·3	413·5
300	478·9	487·4	454·8
400	518·4	527·5	492·3
500	555·1	564·7	527·4
600	589·3	599·4	559·9
700	621·5	632·3	590·8
800	651·7	663·0	619·8
900	680·8	692·3	647·3
1000	708·4	720·6	674·7

* Room temperatures as follows: Air 15·7° C.; Nitrogen 16·7° C.; Oxygen 16·5° C.

TABLE V.

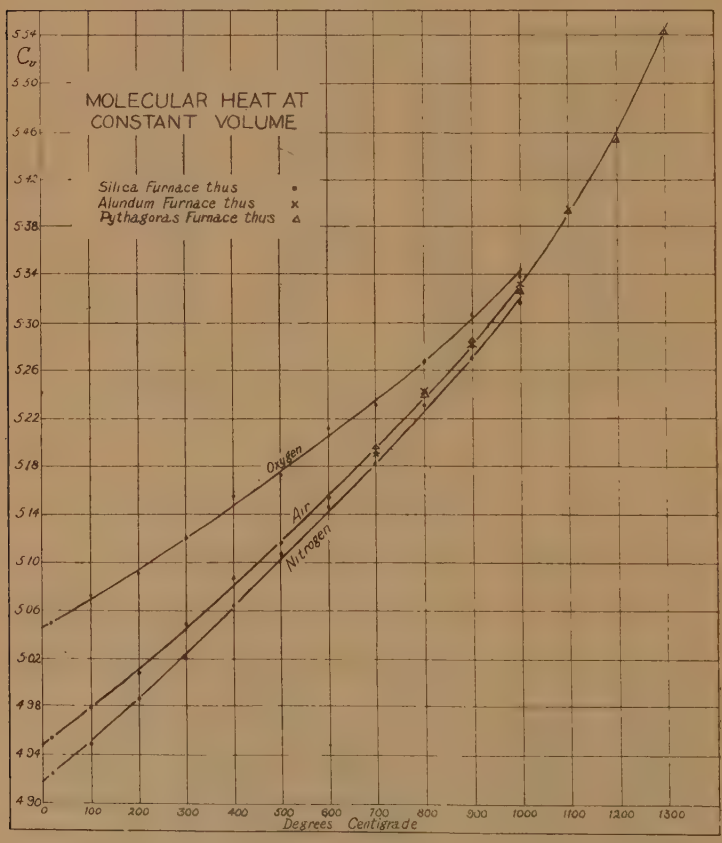
Values of the Physical Constants employed.

Constant.	Gas.		
	Air.	Nitrogen.	Oxygen.
Molecular weight, M	28·98	28·02	32·00
Critical temperature, T_c ...	132·6	126·5	154·25
Critical pressure, p_c	39·3	33·0	50·2
Viscosity at 0° C., η_0	0·000176	0·000167	0·000193
Density at 0° C., ρ_0	0·001293	0·001251	0·001429
$\epsilon = \kappa/c_v\eta$	1·772	1·765	1·867
Ratio, c_p/c_v	1·403	1·405	1·395
Sutherland constant, S ...	119·4	113	132
Thermal conductivity, κ.	$0{\cdot}0_4522$	$0{\cdot}0_452$	$0{\cdot}0_457$
Specific heat, c_v (approx.)	0·1701	0·1760	0·1582
The gas constant, R	$8{\cdot}3157\times10^7$ ergs per °C., or 1·9875 cals. per gm. mole.		

range by the method already described. Table V. gives the values of the various physical constants used in the calculation of the factors required to reduce the experimental results.

If the constants in Table V. are used, the values given in Table VI. are obtained. Equation numbers at the heads

Fig. 1.



of the columns refer to equations fully explained in the previous paper. Berthelot's Equation of State has been used throughout.

From the values given in Tables IV. and VI. the results given in Table VII. are obtained.

The values of C_v are given graphically in fig. 1, which, in

Table VI.

Constants for Air, Nitrogen, and Oxygen.

Temp. °0 C.	Air.			Nitrogen.			Oxygen.		
	ϕ by (2).	$C_p - C_v$ by (3).	Eqn. 81 †.	ϕ by (2).	$C_p - C_v$ by (3).	Eqn. 81 †.	ϕ by (2).	$C_p - C_v$ by (3).	Eqn. 81 †.
0 ...	1·00072	1·997	—	1·00057	1·998	0·52	1·00145	1·999	—
Room *.	1·00044	1·996	0·561	1·00020	1·996	0·56	1·00105	1·998	0·565
100 ...	0·99969	1·991	0·707	0·99955	1·991	0·700	1·00003	1·992	0·709
200 ...	0·99947	1·989	0·867	0·99935	1·989	0·859	0·99967	1·990	0·861
300 ...	0·99944	1·989	1·020	0·99933	1·988	1·008	0·99957	1·989	1·026
400 ...	0·99945	1·988	1·165	0·99937	1·988	1·151	0·99956	1·988	1·161
500 ...	0·99949	1·988	1·306	0·99941	1·988	1·289	0·99957	1·988	1·317
600 ...	0·99953	1·988	1·442	0·99946	1·988	1·432	0·99960	1·988	1·455
700 ...	0·99956	1·988	1·573	0·99950	1·988	1·553	0·99962	1·988	1·590
800 ...	0·99959	1·988	1·702	0·99954	1·987	1·679	0·99965	1·987	1·719
900 ...	0·99962	1·987	1·827	0·99957	1·987	1·803	0·99967	1·987	1·847
1000 ..	0·99965	1·987	1·950	0·99960	1·987	1·923	0·99969	1·987	1·971
1100 ...	0·99967	1·987	2·070						
1200 ...	0·99969	1·987	2·188						
1300 ...	0·99971	1·987	2·304						

* Room temperatures as given in Table IV.
† See p. 293 of the previous communication.

Table VII.

C_v, C_p and C_v/C_p for Air, Nitrogen, and Oxygen up to 1000° C.

Temp. °C.	Air.			Nitrogen.			Oxygen.		
	C_v.	C_p.	C_p/C_v.	C_v.	C_p.	C_p/C_v.	C_v.	C_p.	C_p/C_v.
Room *.	4·952	6·948	1·4029	4·923	6·919	1·4054	5·049	7·046	1·3955
100 ...	4·978	6·969	1·4000	4·948	6·939	1·4024	5·072	7·064	1·3928
200 ...	5·006	6·995	1·3974	4·987	6·976	1·3989	5·089	7·079	1·3910
300 ...	5·048	7·037	1·3939	5·019	7 008	1·3962	5·120	7·108	1·3884
400 ...	5·087	7·075	1·3908	5·068	7·056	1·3923	5·158	7·152	1·3850
500 ...	5·117	7·105	1·3885	5·111	7·099	1·3890	5·174	7·162	1·3842
600 ...	5·156	7·144	1·3855	5·148	7·136	1·3861	5·216	7·204	1·3811
700 ...	5·190	7·178	1·3830	5·177	7·165	1·3839	5·232	7·220	1·3799
800 ...	5·246	7·234	1·3789	5·234	7·221	1·3797	5·270	7·258	1·3771
900 ...	5·280	7·267	1·3764	5·282	7·269	1·3763	5·310	7·297	1·3742
1000 ...	5·323	7·310	1·3734	5·317	7·304	1·3738	5·335	7·322	1·3721

* Room temperatures as given in Table IV. The results are in all cases given to one place of decimals further than that for which validity is claimed.

the case of air, shows also the results of some further measurements to be described later.

From the smoothed curves of fig. 1 the following values (Tables VIII. and IX.) have been deduced :—

TABLE VIII.

Molecular Heats at Constant Volume.

Temp. °C.	Air.	Nitrogen.	Oxygen.
0	4·95†	4·92	—
Room*	4·95	4·92	5·05
100	4·98	4·95	5·07
200	5·01	4·99	5·09
300	5·04	5·02	5·12
400	5·08	5·06	5·15
500	5·12	5·10	5·18
600	5·16	5·14	5·21
700	5·20	5·18	5·24
800	5·24	5·22	5·27
900	5·28	5·27	5·30
1000	5·33	5·32	5·34
1100	5·39	—	—
1200	5·46	—	—
1300	5·54	—	—

TABLE IX.

Molecular Heats at Constant Pressure.

Temp. °C.	Air.	Nitrogen.	Oxygen.
0	6·94†	6·92	—
Room*	6·95	6·92	7·05
100	6·97	6·94	7·06
200	7·00	6·97	7·08
300	7·03	7·01	7·11
400	7·07	7·05	7·14
500	7·11	7·09	7·16
600	7·15	7·13	7·19
700	7·19	7·17	7·23
800	7·23	7·20	7·26
900	7·27	7·26	7·29
1000	7·32	7·30	7·32
1100	7·38	—	—
1200	7·44	—	—
1300	7·53	—	—

* Room temperatures as given in Table IV.

† From the assumed velocity at 0° C.; V=331·4 m./sec.

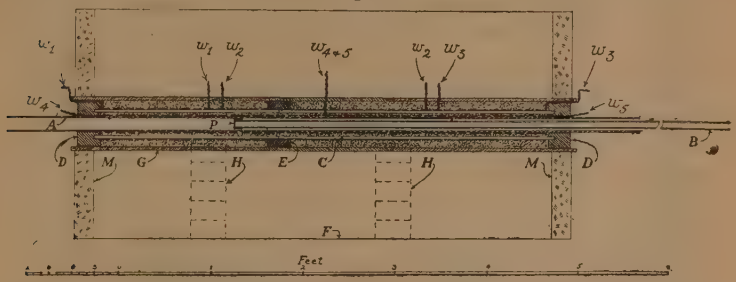
Measurements at Temperatures above 1000° C.

Experimental data for specific heats in the temperature region between 1000° C. and 2000° C. are very scanty. Above this temperature interval measurements can be made by explosion methods. Apparatus can be devised so that most of the other methods of experiment may be used for moderate temperatures approaching 1000° C.

A furnace capable of being maintained at temperatures over 1000° C. is obviously the only modification required before the method already described can be extended. Attempts were first made to use alundum tubes with windings of pure platinum. These failed for several reasons, although results, tabulated later, were obtained from 700° C. to 1100° C.

It was impossible to obtain alundum tubes in lengths greater than three feet. The consequent joints and the high coefficient of thermal expansion of alundum caused

Fig. 2.



mechanical difficulties too great to be overcome in a furnace six feet long. In addition, alundum is so extremely porous that it is necessary to surround the alundum tube containing the gas with an outer jacket of fireclay, so that the furnace tube could be surrounded by a layer of the gas under investigation. A further drawback was the roughness of the inner walls of the furnace tube. Until these had been polished with a carborundum mop it was impossible to make satisfactory measurements. The intensity of the sound-waves was reduced almost to nothing by the time they had reached the centre of the furnace. At a temperature just above 1100° C. the forces of expansion caused the inner tube to fracture in several places. The furnace was dismantled and a new one designed to incorporate several improvements suggested by experience.

A section of the new furnace drawn to scale is shown in fig. 2. The central tube, A, is 2100 cm. long, has a bore

of 4 cm. and a wall thickness of 0·5 cm. It was made of "Pythagorascompo" by W. Haldenwanger of Spandau. The tube had a smooth semi-glazed inner surface, was perfectly straight, of circular cross-section, and would stand a working temperature of 1650° C. At 1200° C. it is practically impervious, even to hydrogen. Hence it was unnecessary to surround the tube with an atmosphere of the gas under investigation. The ends could therefore be left to slide freely in fireclay collars, D, D, so that no strain due to expansion or contraction occurred.

Surrounding this tube was a three-inch bore tube, C, of alundum which carried a second, booster, winding of platinum. Alundum was employed here because this tube, which was in two lengths, was recovered intact from the previous furnace. Recesses in the collars, D, D, supported the ends of this tube concentrically with the inner tube whilst the junction of the two pieces was carried by a fireclay ring, E. Surrounding and supporting the whole was a heavy fireclay tube, G, of six-inch bore made by the Morgan Crucible Company of Battersea. This outer tube was in three sections supported by asbestos brick pillars, H, H, at the junctions. Each section was slit longitudinally into two halves to facilitate assembly of the furnace.

The resistor of the furnace was pure platinum ribbon of cross-section 1 in. × 0·001 in. To wind the inner tube, two lengths of twelve feet of this material were used, the central ends being brought out to a common terminal. For the loan of this platinum and for making necessary repairs we are much indebted to Messrs. Johnson & Matthey.

Splitting the windings enabled the temperature of each half of the furnace to be adjusted independently and current to be used economically. Leads from the ribbon consisted of six strands of 26 S.W.G. platinum wire welded in six different places to the end inch of the ribbon. The six wires were twisted together and brought out as one wire, which was long enough in all cases just to extend for one inch beyond the outer fireclay tube. To extend these leads to terminals on the outer furnace casing, copper rods 3/8 in. diameter were used, the platinum being clamped into a hole drilled for one inch into the end of the rods. The sectional drawing shows how the windings and leads were spaced. An accurately-measured spacing of 5/16 in. between turns was allowed on all windings.

The cascade winding on the alundum tube consisted of two lengths of 10 ft. 4½ in. and one length of 20 ft. 9 in. of ribbon similar to that used on the inner tube. The long length

covered the centre half of the furnace, whilst the two end quarters were separately wound. Experience had shown that with such an arrangement of windings uniform temperatures could be obtained along the whole furnace tube. More heat is required near the ends of the furnace to balance the greater heat-loss. The leads were made exactly as for the centre heating coils, and are shown in fig. 2.

As a further control to balance end-losses, two heaters of nichrome strip wound on alundum formers were inserted near the ends of the furnace. These are not shown on the drawing, but each was wound on a former measuring six inches long and having a bore of five inches. This was fitted over the alundum tube carrying the second platinum winding, but inside the fireclay tube. Each heater was wound with about six yards of 0·0625 in. × 0·006 in. nichrome strip, and was capable of dissipating 400 watts per second.

The platinum windings were coated with a thin cement of pure alundum, dried and recoated, the operation being repeated until a uniform coating several millimetres in thickness was obtained. The annular spaces between the inner and central, central and outer tubes were filled with alundum grain. In the previous furnace the space next to the outer fireclay tube had been left filled only with the gas under investigation. This was done partly to prevent contamination by the atmosphere of the gas used, and partly to ensure more uniform distribution of temperature by convection and diffusion effects. It was found, however, that the furnace functioned much better when the second set of windings was well lagged.

The whole core of the furnace was held concentrically in a large rectangular outer casing by means of the asbestos brickends, M, M. The outer casing (2 ft. 6 in. × 2 ft. 6 in. × 5 ft. 4½ in.) consisted of a heavy iron frame lined with uralite boards. The whole of the remaining space inside the box was filled with lumps of crude bauxite. Owing to the weight of lagging—nearly one ton—the bottom framework of the furnace must consist of I-iron of cross-section at least 4 in. × 2 in. It was found that L-iron slowly twists and sags, with consequent strain on the furnace tube.

A twelve-kilowatt, low-voltage, shunt-wound dynamo supplied the energy for the furnace. Each of the five platinum heating-coils was arranged in a separate circuit, with the exception of coils w_1 and w_3 (see fig. 2), which were run in series. When necessary a shunt resistance could be placed across one of these coils by direct connexion to the

furnace terminals. Adjustment of the end temperatures was, however, more easily effected by using the nichrome end boosters, which could be run from the 240-volt D.C. power circuit. Each platinum winding had as a controlling resistance a six-step series of one-ohm coils in series with a six-step vernier which had a total resistance of one ohm. The resistances were made of 12 S.W.G. nichrome wire. This fine adjustment of the resistance, together with the variable voltage of the dynamo, gave excellent control of the furnace temperature. A total of 3·3 kw. was required to reach a uniform temperature of 1000° C. throughout the furnace tube.

Temperature measurements were made by means of a Foster Optical Pyrometer of the disappearing filament type. Experiments kindly undertaken for us by the Foster Instrument Company of Letchworth showed that the instrument would record temperatures accurately if sighted down the piston tube and focussed on the piston face. When the piston is pushed into the furnace, it is necessary to read a temperature near the left-hand side of the furnace (see fig. 2) whilst sighting through the central part of the furnace. The latter is generally at a slightly higher temperature than that of the ends of the furnace. Messrs. Foster & Company carried out experiments on a disk maintained at 850° C. Direct readings were made and also readings when the pyrometer was sighted through a tube six feet long and one inch bore, with its central part maintained at 1200° C. Both readings were the same, as was also the reading through the tube after it had been cooled down. The differences of temperature used in these experiments were very much greater than any which would normally occur. It was found, however, that a tube of six feet length should not be less than $\frac{3}{4}$-inch bore if the readings were to be consistent. The piston tube, B (fig. 2), was therefore designed to have a bore of 24 mm. The wall thickness was 4 mm. and the length 2 metres. It was made of Pythagorascompo, and the piston head, P, was formed and made in one piece with the tube. As in the previous work, the face of the piston was made as thin as possible to reduce the temperature lag of the back upon which the pyrometer was sighted.

The pyrometer and the open end of the piston tube were rigidly fixed to a sliding platform, so arranged that the pyrometer was always focussed on the back surface of the piston face. The whole platform was arranged to slide by means of a three-point bearing on two steel rods placed parallel to the axis of the furnace. A pointer attached to

the platform showed the scale-reading corresponding to the position of the piston in the furnace.

The end fittings of the furnace were of the same pattern as those described in the previous communication *. The only difference was that the piston fittings had to be enlarged. Water-cooling was arranged on the syphon system from a ten-gallon drum placed on top of the furnace. This was done to be independent of an intermittent water-supply.

With the silica apparatus, contraction of the piston rod as it was pulled out of the furnace could be neglected. A maximum correction of 0·7 mm. would be necessary if the whole 1·5 metre length of the piston were pulled out at 1000° C. and cooled to 20° C., assuming the coefficient of expansion of silica to be $5{\cdot}0 \times 10^{-7}$. At the higher temperatures the full length of the scale could not be used, so that the maximum correction would be of the order 0·5 mm., which is the limit to which measurements could be made at these temperatures.

The coefficient of linear expansion of alundum is $4{\cdot}8 \times 10^{-6}$, and that of pythagoras material is of the same order. The necessary correction was made directly at each reading, since a known length of the tube was pulled out. After passing the water-cooled gland and remaining exposed to the air for the time required for each measurement, the rod was practically at room temperature. The temperature drop was assumed to be from the temperature actually measured at the particular point down to room temperature. Since all the movements are of the same length and the variations in temperature along the furnace are small, this method gives the corrections to well within the required limits. The cooled length was measured from the gland to the reading index. On the furnace side of the gland the temperature equilibrium remains the same throughout a series of measurements, so that no contraction or expansion of the rod occurs in this region. This assumption is based on the behaviour of the telephone end of the furnace, where any disturbance of temperature equilibrium would be shown by a changed zero reading. This point has been fully discussed elsewhere †.

The makers state that the coefficient of linear expansion of pythagorascompo is the same as that of hard porcelain. Mellor and also Rieke state that the higher the firing

* Phil. Mag. iii. p. 273 (1927).

† See p. 283 of the previous communication.

temperature the lower is the coefficient of expansion of porcelains. Figures given by Holborn and Grüneisen, Bedford, and Rosenthal for Berlin porcelain vary between $3{\cdot}03 \times 10^{-6}$ and $3{\cdot}6 \times 10^{-6}$, whereas Scheel gives $2{\cdot}8 \times 10^{-6}$. A value of $3{\cdot}5 \times 10^{-6}$ has been taken for our calculations, since the coefficient of expansion increases slowly with temperature, but will probably be slightly lower than that of hard porcelain, since pythagorascompo is fired at a very high temperature.

The maximum correction from room temperature to the maximum temperature reached (just above 1300° C.) is therefore about 6·8 mm. for the pythagorascompo tube and about 9·0 mm. for the alundum tube, allowing contraction on the full 1·5 metre length. The need for these corrections is obvious.

Results.

After initial calibrations of the furnace tube, experiments with both the alundum and the pythagorascompo furnaces were begun at 700° C. to obtain an overlap to the temperature region already explored.

Measurements with the alundum tube had only progressed as far as 1100° C. when the furnace tube collapsed under the strain due to expansion.

The second furnace tube was quite successful, and measurements had been made up to 1300° C., when the piston tube was accidentally broken. Owing to labour troubles in the German porcelain industry a long wait for replacements ensued, so that it is thought advisable to publish results as far as they go. There seems to be no reason why this method of experiment should not be successful to the limit of the apparatus. The furnace tube will stand a working temperature of 1650° C., and may even be used for a short time up to 1700° C. With a closely-adhering layer of alundum cement to prevent volatilization, the platinum should remain intact at 1650° C.

Table X. compares the velocities of sound obtained :

1. In the old silica furnace.
2. In the alundum furnace.
3. In the pythagorascompo furnace.

The corresponding values of C_v are tabulated in Table XI. and are compared graphically in fig. 1.

Of the three series that with furnace 2 is considered the least reliable, since only a few sets of measurements were

taken before the furnace collapsed. Final values of C_v and C_p have been added to Tables VIII. and IX.

Fig. 1 shows the excellent agreement between the three independent sets of measurements. There is a tendency for the values of C_v to rise more sharply from 1000° C. upwards. This is confirmed by the values calculated by one of the authors * from considerations of gaseous equilibria. The

TABLE X.

True Velocities of Sound in Air in metres per second.

Temp. °C.	1.	2.	3.
700	621·51	621·57	621·42
800	651·71	651·71	651·75
900	680·77	680·74	680·70
1000	708·42	708·24	708·36
1100	—	734·40	734·39
1200	—	—	759·54
1300	—	—	783·18

TABLE XI.

Values of C_v for Air.

Temp. °C.	1.	2.	3.
700	5·190	5·187	5·197
800	5·246	5·246	5·243
900	5·280	5·282	5·284
1000	5·323	5·331	5·326
1100	—	5·394	5·393
1200	—	—	5·453
1300	—	—	5·544

curve of fig. 1 is similar to those for oxygen and nitrogen in fig. 2 of the above reference.

The Tube Correction.

Our method of calculation has recently been criticised by Cornish and Eastman †, who state that our results are worthless unless recalculated. They state that an explanation of

* Trans. Far. Soc. xxii. p. 377 (1927).
† J. A. C. S. l. p. 627 (1928).

the results may be that our frequency was not correctly determined. As has already been described *, the frequency of our oscillator was determined for us at the National Physical Laboratory. A copy of the tables of results included with the certificate is set out in the reference given. In addition, a steel bar standard was made up and calibrated at the National Physical Laboratory. This standard had a frequency very near that of the oscillator. The exact frequency of the latter could be estimated to one part in ten thousand in a few seconds by comparison with the steel standard. The standard wave-meter referred to was used to check the approximate frequency before the oscillator was sent to be calibrated.

In the later work with the alundum and pythagorascompo furnaces, the oscillator was modified in detail and all switches excluded. The changes reduced the total capacity of the circuit, causing the frequency to rise slightly. For the new frequency another steel standard was prepared. The oscillator used by Cornish and Eastman is essentially the same as ours except that less precautions were taken to ensure constant frequency. They used ordinary wireless condensers to obtain their capacity. These are relatively unstable and usually have a considerable temperature coefficient. No mention is made of any precautions taken to ensure a constant inductance. The calibration tables for our instrument showed that it is essential to maintain the anode current of the valve constant if a constant frequency is necessary. For this purpose we included a vernier resistance and a milliameter in our filament circuit. In Cornish and Eastman's work this point seems to have been overlooked. Cornish and Eastman's determination of frequency seems to involve the counting of beats up to a possible maximum of 600 in two minutes. We have not attempted to count this number of beats in the time stated.

Since the tube correction in Cornish and Eastman's work agrees, by coincidence, with the theoretical equation given by Kirchhoff and Helmholtz, the former workers claim "overwhelming evidence" that the equation is universally true. Only a summary of the evidence against this claim need be given here, as the fallacy of the Kirchhoff-Helmholtz equation is too well established to need discussion. There is no evidence in the literature that *large* amounts of dust were used, as stated by Cornish and Eastman, unless for the express purpose of determining the effect of large

* Phil. Mag. iii. p. 273 (1927) (see p. 279 for tables).

excesses of dust. Kundt * introduced up to 10 gm. of lycopodium powder in some of his experiments. The effect of excess dust is quite small. Schneebeli †, Seebeck ‡, Kayser §, Müller ||, and Sturm ¶ all obtained proof that the law of Kirchhoff and Helmholtz does not hold. In addition, we have Kirchhoff's own admission that the law could not hold unless the tube were perfectly smooth. Thiesen ** has given a special treatment for the case of closed resonators. The factors obtained by Dixon and his co-workers †† also show that the Kirchhoff–Helmholtz equation has no general application. Finally, our own work on this subject has satisfied us that the only possible way to obtain an accurate tube correction is to determine it experimentally. This we have done throughout all our work, a point which Cornish and Eastman have ignored entirely.

To determine this correction the wave-length of sound in pure air at an accurately-measured temperature at, or near, that of the room is determined. Since the frequency of the note is known, the product *frequency* × *wave-length* gives the apparent velocity of sound in air at the measured temperature. Great care must be taken to measure actually the temperature within the furnace tube, since the amount of lagging round the furnace renders it useless simply to measure room temperature. The lagging renders the tube immune from sudden small changes in room temperature. A calibrated thermometer pushed down the piston tube was used to measure this temperature. A thermometer with moderate lag was chosen so that in the few seconds required to withdraw it and read the temperature the error could not be greater than 0·1° C.

The true velocity of sound in pure air at the measured temperature was then calculated from the velocity at 0° C. on the assumption that velocities are proportional to the square root of the absolute temperature. Strictly speaking, the velocities are proportional also to $\sqrt{\gamma}$, but the difference for such small temperature differences is negligible. Hence the difference *True Velocity—Actual Velocity* is accurately known.

* Pogg. *Annalen*, cxxxv. pp. 337 & 527 (1868).
† Pogg. *Annalen*, cxxxvi. p. 296 (1869).
‡ Pogg. *Annalen*, cxxxix. p. 104 (1870).
§ *Ann. Phys.* ii. p. 218 (1877).
|| *Ann. Phys.* xi. p. 331 (1903).
¶ *Ann. Phys.* xiv. p. 822 (1904).
** *Ann. Phys.* xxiv. p. 401 (1907).
†† Proc. Roy. Soc. A, c. p. 1 (1921); cv. p. 199 (1924).

Our tube correction is of the form *

$$V' = V[1-ck], \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

V' = the measured velocity in the tube,
V = the true velocity in free air,
k = the tube constant,
c = a factor given by

$$c = \sqrt{\frac{\eta_0 T\left[1+\frac{S}{273}\right]\sqrt{1+\frac{t}{273}}}{\rho_0 \times 273\left[1+\frac{S}{T}\right]}}\left[1+\sqrt{\epsilon}\left[\frac{\gamma-1}{\sqrt{\gamma}}\right]\right] \quad . \quad . \quad . \quad (2)$$

in which

η_0 = the viscosity at 0° C.,
ρ_0 = the density at 0° C.,
T = the absolute temperature,
t = the temperature in degrees centigrade,
S = the Sutherland constant,
$\epsilon = \kappa/\eta c_v$ = thermal conductivity / (viscosity × sp. ht.),
$\gamma = C_p/C_v$ = the ratio of the specific heats.

Helmholtz and Kirchhoff † represented the velocity of sound in tubes by

$$V' = V[1-c/2r\sqrt{(\pi N)}], \quad . \quad . \quad . \quad . \quad (3)$$

where

V = the true velocity in the free gas,
V' = the velocity in the tube,
N = the frequency of the note used,
r = the radius of the tube.

Helmholtz states that the constant c is the viscosity of the gas, but, according to Kirchhoff, c depends on the heat-exchange between the gas and the walls of the tube, and may be represented by

$$c = \sqrt{(\alpha)} + [V/b - b/V]\sqrt{\beta},$$

in which

b = the Newtonion velocity of sound, $\alpha = \eta/\rho$, and $\beta = \kappa/\rho c_v$, where η is the coefficient of viscosity, κ the coefficient of

* See 'Specific Heats of Gases,' pp. 50–55.
† Pogg. *Annalen*, cxxxiv. p. 177 (1868).

thermal conductivity, ρ the density of the gas, and c_v the specific heat at constant volume. Substituting these values for α and β above, writing $\epsilon=\kappa/\eta c_v$, and remembering that

$$V/b = \sqrt{C_p/C_v} = \sqrt{\gamma},$$

we have

$$c = \sqrt{(\eta/\rho)}\left[1+\sqrt{\epsilon}\left(\frac{\gamma-1}{\sqrt{\gamma}}\right)\right]. \quad . \quad . \quad . \quad (4)$$

The variation of η with temperature is then assumed to be given by Sutherland's equation *, and the density to be inversely proportional to the absolute temperature. When these additions are made, equation (2) above is obtained. This equation, which is Kirchhoff's equation neglecting only the effect of r and of N, takes no account of the nature of the inner surface of the tube nor of the thermal properties of the material of which it is made. Sturm (*loc. cit.*) showed definitely that the material of which the tube is made affects the velocity of sound in it. The experimental constant k (equation (1)) is necessary to correct for the effect of the various factors which cannot be determined theoretically. The assumption must then be made that the tube correction does not depend on the temperature. This assumption admittedly contains the weakness that the thermal conductivity of the tube, and hence the heat-exchange between it and the gas, may change with temperature. The difference must be extremely small, but it is unfortunate that sufficient thermal data are not available to apply the correction. It seems reasonable to assume that the nature of the inner surface of the tube does not change at temperatures well below the softening point of the material of which it is made.

For the various tubes used the following values of k were found :—

Tube.	A.	B.	C.	D.
k	0·0168	0·0186	0·00713	0·00136

Tube A. The short silica tube first used (see Trans. Far. Soc. xviii. p. 386, 1923). With this furnace an oscillator having a frequency of 2947 vibrations per second was used.

Tube B. The long silica tube used for experiments up to 1000° C. (see Phil. Mag. iii. p. 273, 1927). The frequencies used in these experiments were between 2992 and 3006 per second, changes being due to renewal of valves. Each frequency was accurately determined for a given anode current

* Phil. Mag. xxxvi. p. 507 (1893).

by the steel bar method as recommended by the National Physical Laboratory. In the experiments on steam, described in the last communication, the tube constant was found to have changed slightly. The change, which was the only one ever recorded throughout this work, may be ascribed to the fact that steam was the last of a series of six gases to be investigated in the same tube. The constant used was 0·0180 instead of 0·0186.

Tube C. The alundum furnace tube, using a frequency of 2992.

Tube D. The pythagorascompo tube, used with slight improvements to the oscillator and a change of frequency to 3018·5 per second.

The values of C_v, plotted in fig. 1, show the results obtained with tubes B, C, and D. Tubes B and C have, respectively, correction factors approximately ten times and three times greater than that demanded by Kirchhoff's formula, whilst that of tube D is less than the theoretical value. From the excellent agreement of the final values of C_v for the three tubes, we thus confirm previous workers' conclusions that the Kirchhoff-Helmholtz formula cannot be applied generally.

The differences in the tube constants can be explained qualitatively by a consideration of the nature of the tubes. The two factors mentioned by Kirchhoff probably account for the greater part of the differences. They are (*a*) the nature of the inner surface of the tube, (*b*) the heat-exchange between the tube and the gas. Tube B was of silica with a glazed inner surface, whilst the surface of C was very rough. Tube D had a very uniform and smooth surface, but was not glazed as in the case of B. The thermal conductivities of the tubes B, C, D are respectively 0·00082, 0·00833, and 0·00169. The measurements are comparative and are taken from the Norton Company's handbook *. Thermal conductivity seems to play a relatively large part. Thus, the excellent surface of the silica tube B is more than counterbalanced by its very low thermal conductivity. Hence a large correction factor. With the alundum tube the thermal conductivity is very high, but the extremely rough and porous surface increased what would otherwise probably have been a very small factor. The pythagorascompo tube—a mixture of aluminium oxide and fireclay—had a conductivity probably greater than that given above, which is the value for fireclay. It had an excellent inner surface. Hence the very small correction factor. The metal tubes used by

* 'Norton Refractory Laboratory Ware,' 1926, p. 9.

Cornish and Eastman would have very high thermal conductivity and presumably a fairly smooth surface. The tube correction thus might easily have coincided with the theoretical value, but coincidence with theoretical values in a single piece of research work does not seem to us sufficient grounds for dismissing as entirely wrong the work of many previous investigators and for claiming overwhelming evidence in favour of the minority. Particularly does this apply when the limitations of the theory were pointed out by its originator.

Summary.

The molecular heats of air, nitrogen, and oxygen have been determined over a temperature 0° C. to 1000° C. by a method depending on the measurement of the velocity of sound in the chemically pure gases. Further measurements for air up to 1300° C. are added, and a reply is given to criticism of the method of determining the tube constant.

Chemistry Department,
East London College,
University of London.

XCI. *The Effect of Refraction on Electron Diffraction.* *By* G. P. Thomson, M.A.*

In a very valuable and important paper on the diffraction of electrons by thin metal films, E. Rupp † considers that his results can be best explained by attributing a refractive index to the metal for electron waves and calculates its value in certain cases. These values have recently been used by Rosenfeld and Witmer ‡ in a theoretical paper. While the hypothesis that a metal shows a refractive index for electrons is intrinsically probable, and seems by far the best way of accounting for some of Davison and Germer's experiments with reflected electrons, it appears that there is an oversight in Rupp's method of calculation which greatly modifies the conclusions which can be drawn from his experiments. The problem is as follows:—Electrons are assumed to be guided by waves whose wave-length in free space is $\lambda = h/nw$. They pass at normal incidence through a thin film of metal and are diffracted by the atoms of the crystals composing it, a pattern being formed analogous to

* Communicated by the Author.
† E. Rupp, *Ann. der Phys.* lxxxv. p. 981 (1928).
‡ Rosenfeld and Witmer, *Zeit. f. Phys.* xlix. p. 534 (1928).

a Debye-Scherrer pattern for X-rays. How will the pattern be modified if the wave-length in the metal is not λ but $\lambda' = \lambda/\mu$ where μ is a quantity analogous to an optical refractive index? When $\mu = 1$ the electrons are reflected whenever they are incident on a crystal plane at an angle θ satisfying Bragg's law

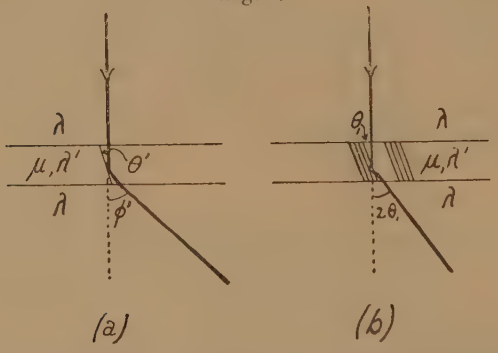
$$n\lambda = 2d \sin \theta,$$

and a diffracted beam occurs with a deviation $\phi = 2\theta$. If $\mu \neq 1$ this becomes (fig. 1, *a*)

$$n\lambda/\mu = 2d \sin \theta',$$

and this is the relation (in my notation) which Rupp uses to find θ' the new angle of reflexion. For the deviation he

Fig. 1.



takes $2\theta'$, and it is here that the error lies. If the wave-length is modified in the metal, there must, by Huyghen's principle, be a bending of the rays on emergence. In the actual case where the incidence is normal there is no bending on entering the metal, but λ becomes λ' and the deviation *in the metal* is $2\theta'$, which is the angle of incidence on the second surface. The angle of refraction ϕ' is given by

$$\sin \phi' = \mu \sin 2\theta'.$$

Comparing with the case where $\mu = 1$,

$$\sin \theta / \sin \theta' = \mu$$

and

$$\sin \phi' / \sin \phi = \mu \sin 2\theta' / \sin 2\theta = \cos \theta' / \cos \theta$$
$$= \sqrt{4\mu^2 d^2 - n^2\lambda^2}/\mu \sqrt{4d^2 - n^2\lambda^2}.$$

Thus for θ, θ' small the effects compensate, and for larger angles the small effect is in the opposite direction to that given by Rupp's calculation.

It has been suggested that the diffraction actually observed in these and similar experiments occurs at the inner surfaces of holes in the metal film (fig. 1, *b*). While holes are undoubtedly present in the films I used, and may have occurred in Rupp's films also (see, for example, Smekal's paper in the 'Transactions of the Volta Centenary' on the imperfection of crystals), it does not seem likely that these really play an important part. If the rays were really reflected from planes parallel to the inner face of one of these holes, the effect of refraction would be expressed by a formula found by Darwin * for the analogous case with X-rays, namely,

$$\theta_1-\theta=\frac{\mu-1}{\sin\theta\cos\theta},$$

where θ_1 is the new glancing-angle outside the metal, and $\mu-1$ is small. Now in my experiments † with electrons of the order of 40,000 volts, θ_1 was of the order $\frac{1}{50}$, thus

$$(\theta_1-\theta)/\theta\sim 50^2(\mu-1).$$

But Bragg's law held in its simple form to better than 1 part in 50, thus

$$|\mu-1|<\frac{1}{50^3}.$$

The theoretical formula

$$\mu=\sqrt{1+\Phi/E},$$

where E the kinetic energy of the electron and Φ the potential of the metal, then gives $|\Phi|<\cdot 7$ volt. This is very small compared with the 18 volts found by Davison and Germer and with any theoretically probable value. In addition there is very little difference between patterns taken with my original films which had obvious holes, and with films which I have been using recently made by spluttering, which appear quite continuous under the microscope.

In criticizing Herr Rupp's calculations of the effect of the refractive index I should like to emphasize that I am not trying to minimize the importance of the exceedingly beautiful work he has done in showing that comparatively slow electrons can show well-marked diffraction patterns through metal films. The supposed effect of refractive index is only a few per cent. in any case, and Herr Rupp himself says

* C. G. Darwin, Phil. Mag. xxvii. p. 320 (1914).

† 'Nature,' cxx. p. 802 (1927); Proc. Roy. Soc. A, cxvii. p. 600 (1928).

that it is on the limit of the accuracy of the experiments. The discrepancy left, when the calculation is made as indicated above, may perhaps be accounted for by a slight systematic error in the measurement of the electron velocities.

Aberdeen,
Sept. 27, 1928

XCII. *Notices respecting New Books.*

Handbuch der Radiologie: *Vierter Band, Dritter Teil.* "*Glühelectroden*," von O. W. Richardson; "*Technische Anwendung der Glühelectroden*," von H. Rukop; "*Flammenleitung*," von Erich Marx. Zweite Auflage. [Pp. xvi+724, mit 190 Figuren und Abbildungen im Text.] (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1927. Price, brosch. M.48; geb. M.50.)

THE third part of the second edition of Bd. iv. of the 'Handbuch der Radiologie' comprises three monographs. The first is a translation, by Prof. A. Karolus, of Richardson's well-known work on the emission of electricity by hot bodies. This has been brought up to date where necessary by a 32 page appendix, contributed by E. Rupp. The second monograph, by Prof. Rukop, written for the new edition of the Handbuch, is an account of the technical applications of thermionic emission. It is naturally concerned to a large extent with the theory and the various practical applications of the triode valve and of tubes with special characteristics—tubes with multiple grids, tubes used in conjunction with magnetic fields, &c. Extending to 138 pages, this monograph deals with the subject in a very comprehensive manner.

The third monograph, by the Editor of the Handbuch, deals with the conduction of electricity in flames. Since the appearance of the first edition, the theory of temperature ionization, advanced by M. N. Saha to explain the phenomena of stellar spectra, has gained general acceptance. This theory was shown by H. A. Wilson and Noyes to be applicable to the problem of conduction in flames. A full account of the theory and of its applications to electrical conduction in flames has been included in the new edition; the theory has enabled some matters, which were controversial at the time of the first edition, to be settled and the relevant sections have therefore been omitted. The monograph provides a valuable summary of the present position of practice and theory with respect to the phenomena of electrical conduction in flames.

Although the process of subdivision has been carried further in the second edition than the first, there does not appear to be any particular advantage in publishing these three monographs in one volume. If each were obtainable separately the sales would undoubtedly benefit.

The Theory of Probability. By the late William Burnside, Sc.D., LL.D., F.R.S. [Pp. xxx+106.] (Cambridge: At the University Press. 1928. Price 10*s.* 6*d.* net.)

The late Professor Burnside became interested in the theory of probability during the period of the war, his first paper on the subject, published in 1918, being concerned with a military question. His interest in the subject grew, and other papers on topics related to the theory of probability appeared from time to time. Finally, he set out to prepare a systematic account of the theory. The draft was completed before a serious illness in 1925; although it contained all the issues which he proposed to discuss, additions and amplifications were intended, but remained unwritten. A number of notes, elucidating or establishing statements in the text were planned: only one was written, and no memoranda were left indicating the nature of the remainder. In these circumstances the draft has been published, under the editorship of Dr. A. R. Forsyth, exactly as it was written and has been prefaced by the obituary notice written by Dr. Forsyth for the Royal Society.

The account of the theory occupies only 100 pages and possesses the conciseness and precision characteristic of Prof. Burnside's writings. In the introductory chapter, the rule for calculating calculable probabilities is properly enunciated, and the method of estimating probability discussed. Direct, indirect and approximate methods of calculating probabilities are dealt with successively, with numerous illustrative examples. Two chapters are devoted to the probability of causes and to probabilities connected with geometrical questions. The final chapters deal with the theory of errors and with Gauss's law of errors. The volume forms a valuable addition to the literature concerned with the theory of probability.

XCIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. v. p. 1263.]

April 4th, 1928.—Prof. J. W. Gregory, D.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

1. 'The Analcite-Syenites and Associated Rocks of Ayrshire.' By George Walter Tyrrell, A.R.C.Sc., Ph.D., F.R.S.E., F.G.S., Lecturer in Geology in the University of Glasgow.

The analcite-syenites of Ayrshire occur in differentiated intrusions along with analcite-olivine-dolerites or crinanites, as stratiform bands, schlieren, and veins. The principal occurrence is at Howford Bridge, Mauchline, where analcite-syenite forms a considerable

part of the sill. In the remaining three described occurrences (Dippol Burn, Trabboch Burn, and Prestwick) the analcite-syenite is restricted to schlieren and veins.

The Howford Bridge, Dippol Burn, and Trabboch Burn occurrences form sills intrusive into the Permian lavas and tuffs of the Mauchline basin; the Prestwick sill is intruded into sediments of Coal-Measure age. They all belong to the widespread suite of analcite-bearing igneous rocks of late-Carboniferous and Permian age in the West of Scotland.

The constituent minerals of these rocks are labradorite, sodic plagioclase, potash-oligoclase, olivine, titanaugite, ægirine, soda-amphiboles, ilmenite, along with analcite and certain zeolites. The most noteworthy mineralogical feature is the abundant occurrence of analcite, thomsonite, natrolite, and prehnite, which must be regarded as late primary crystallizations from the magma.

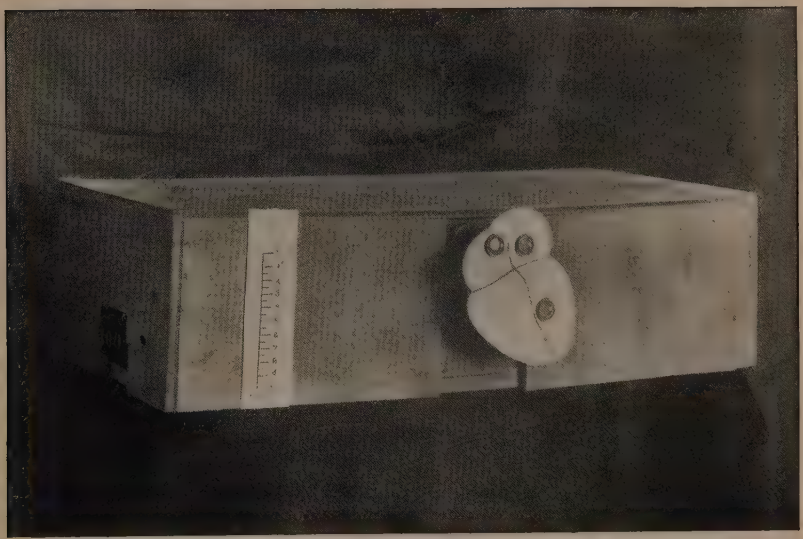
Petrographically the rocks are divided into: (A) Olivine-analcite-dolerite (crinanite), constituting the major portions of all the described occurrences; (B_1) Analcite-syenite, a coarse-grained, comparatively basic type, which occurs as bands, schlieren, and veins; and (B_2) Analcite-syenite, a perfelsic type, rich in analcite and other zeolites, and with abundant ægirine and soda-amphibole. This variety is found chiefly as veins. Analyses of crinanite and analcite-syenite illustrate the chemistry of these rocks.

The analcite-syenite differentiate is found towards the interior parts of the sills. The petrographical variations within the various intrusive bodies are ascribed to simple crystallization-differentiation aided by the gravitative settling of titanaugite-ilmenite intergrowths. Several reaction-series, continuous and discontinuous, have been traced, and these have been combined in a Goldschmidt diagram showing at one and the same time the parallel courses of crystallization and differentiation. It is shown that a certain amount of lime is probably stored up in the residual liquor, along with the usual soda, potash, silica, water, and volatile constituents, leading to the final crystallization of analcite, soda-lime zeolites, and prehnite.

An hypothesis for the development of schlieren and veins in the sills under discussion by the effects of the varying incidence of the pressure due to the superincumbent column of rock, upon a crystal-mesh filled with interstitial liquid, is framed. The liquid is believed to be progressively driven towards the centre of the sill, and also laterally towards those places where the pressure is compensated in various ways, so that free contraction of the crystallizing mass can take place. The great development of analcite-syenite within the Howford Bridge sill is shown to be concomitant with the impoverishment of the associated crinanite in analcite; whereas in the other three sills, which contain relatively small developments of analcite-syenite, the crinanitic portions are relatively rich in analcite.

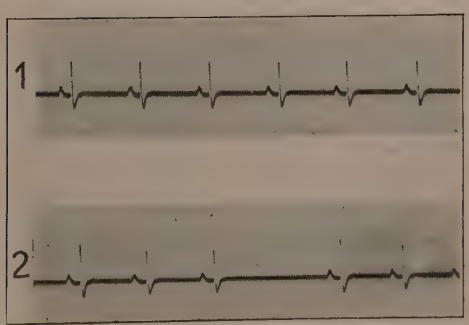
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Fig. 4.



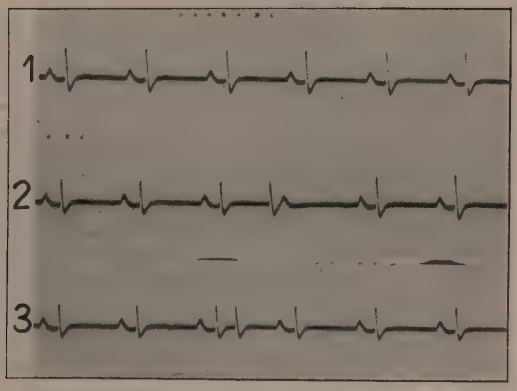
Outside view of model.

Fig. 7.



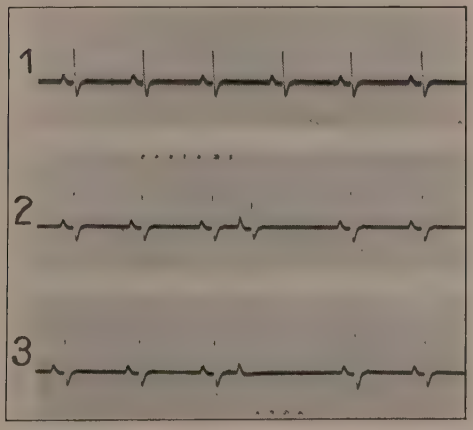
1. Normal heart beat.
2. Sino-auricular block.

Fig. 8.



Ventricular extrasystolæ:—1, normal heart beat; 2, late ventricular extrasystole resulting in the ventricle being in the refractory state when the next following normal stimulus arrives from the auricle; 3, early ventricular extrasystole; here the ventricle is *not* any more in the refractory period when the next following normal stimulus arrives from the auricle and thus an *interpolated ventricular* systole is obtained.

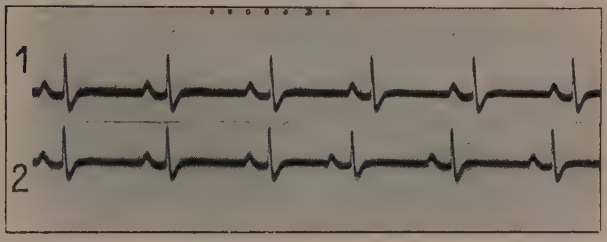
Fig. 9.



1. Normal heart beat.
2. Auricular extrasystole (with the ventricle responding).
3. Auricular extrasystole (ventricle still in refractory period).

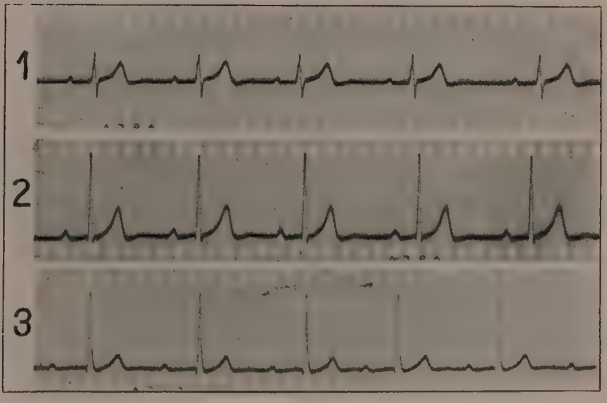
Note the increased amplitude of the following normal ventricular systole.

Fig. 10.

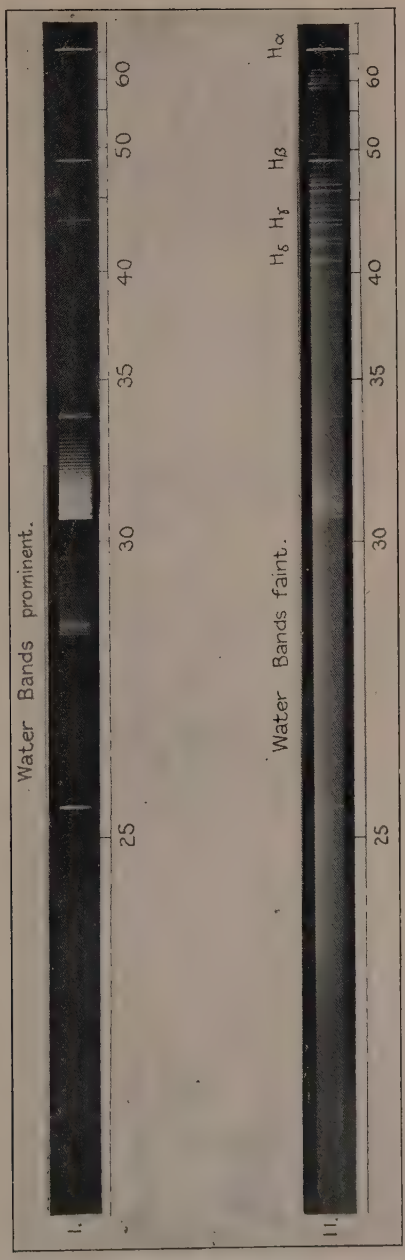


1. Normal heart beat.
2. Sinus extrasystole disturbing the whole heart rhythm.

Fig. 11.



Electrocardiogram of the real heart taken in the standard positions 1, 2, and 3 with the aid of a special very low frequency amplifier and a Cambridge oscillograph.



THE CONTINUOUS SPECTRUM OF HYDROGEN.

Fig. 1.

Fig. 2.

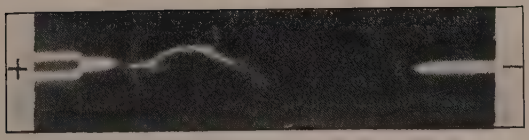
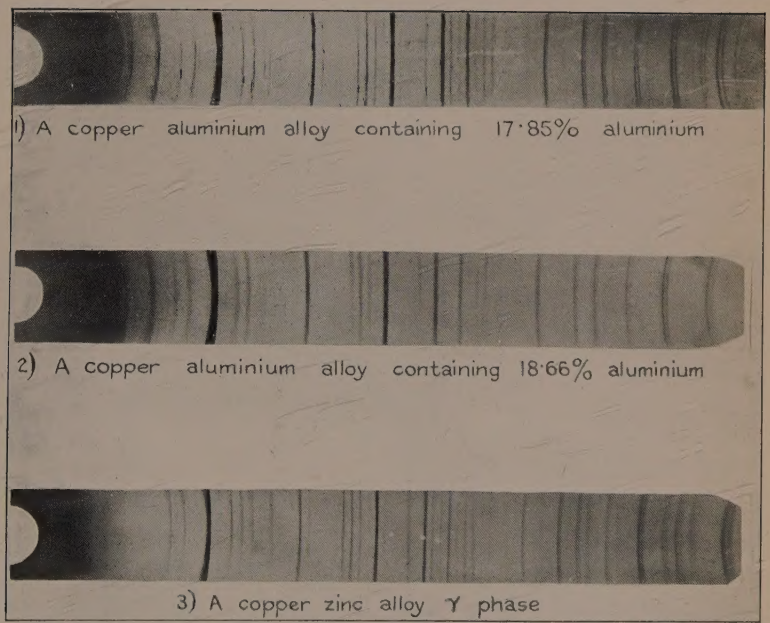


Fig. 3.


1) A copper aluminium alloy containing 17·85% aluminium
2) A copper aluminium alloy containing 18·66% aluminium
3) A copper zinc alloy γ phase

Powder Photograms of δ Cu–Al Alloys compared with γ Cu–Zn.

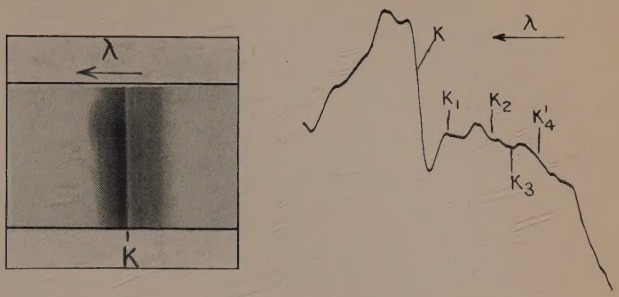


FIG. 1.—K Absorption of Fe in FeS_2 crystal.

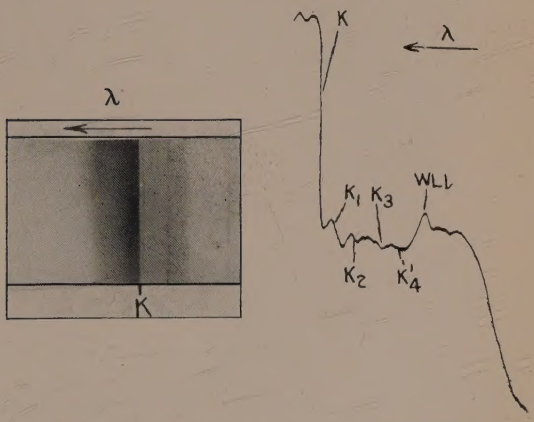


FIG. 2.—K Absorption of Fe in screen of Fe_3O_4.

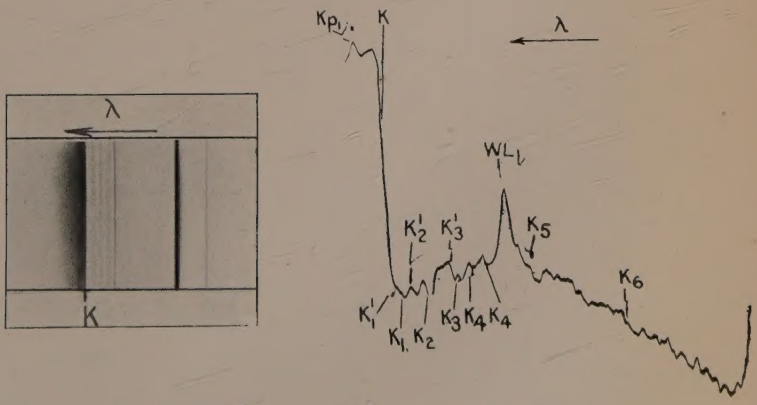


FIG. 3.—K Absorption of Fe in screen of metallic iron.